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9. Molecular Thermodynamic Modeling of Fluctuation Solution Theory Properties

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Abstract

Fluctuation Solution Theory provides relationships between integrals of the molecular pair total and direct correlation functions and the pressure derivative of solution density, partial molar volumes, and composition derivatives of activity coefficients. For dense fluids, the integrals follow a relatively simple corresponding-states behavior even for complex systems, show well-defined relationships for infinite dilution properties in complex and near-critical systems, allow estimation of mixed-solvent solubilities of gases and pharmaceuticals, and can be expressed by simple perturbation models for densities and gas solubilities, including ionic liquids and complex mixtures such as coal liquids. The approach is especially useful in systems with strong nonidealities. This chapter describes successful application of such modeling to a wide variety of systems treated over several decades and suggests how to test Equation of State mixing rules.

9.1 Introduction

Among the many thermodynamic properties that can be treated by Fluctuation Solution Theory, those for mixtures have had the longest history. Chapter 1 develops the relations from fluctuations in the grand ensemble for partial derivatives of the mole numbers with chemical potentials at fixed temperature, volume, and other chemical potentials in terms of integrals of pair total correlation functions. Matrix inversions and thermodynamic manipulations connect these integrals to partial derivatives of the pressure with respect to mole numbers which are related to the partial molar volume, and derivatives with respect to density, that are related to the isothermal compressibility. Expansions of these properties about infinitely dilute solution were the focus of the seminal paper of Kirkwood and Buff (Kirkwood and Buff 1951), and further works by Buff and coworkers where partial molar energies and heat capacities (Buff and Brout 1955), as well as perturbation theory for corresponding states (Buff and Schindler 1958), were developed. Pearson and Rushbrooke (Pearson and Rushbrooke 1957) further extended the relations by involving the direct correlation function to provide closure relations for correlation function integrals.

After some time, the basic formulation for activities and compressibilities was redone for the whole range of concentrations and for expressions that avoided matrix complexities by involving integrals of direct correlation functions (O'Connell 1971b). It was noted much later that for molecular systems, these relations depended on the applicability of the “weak approximation” for angle-dependent intermolecular forces (Gray and Gubbins 1984; O'Connell 1994). In the absence of molecular simulations, this justified the successful applications of early works that used molecular theory (Gubbins and O'Connell 1974) and practical (Brelvi and O'Connell 1972,

1975b, 1975a; Brelvi and O'Connell 1975c) perspectives, mainly via corresponding states. This FST approach was extended to correlate densities and activities of supercritical components in liquids and liquid mixtures (Mathias and O'Connell 1979; Mathias and O'Connell 1981; O'Connell 1981; Perry and O'Connell 1984) and of aqueous electrolyte solutions (Cabezas and O'Connell 1986; Cooney and O'Connell 1987; Perry, Cabezas, and O'Connell 1988; O'Connell, Hu, and Marshall 1999). Properties of near- and supercritical systems were also well-described (Campanella, Mathias, and O'Connell 1987; O'Connell, Sharygin, and Wood 1996; Liu and O'Connell 1998; O'Connell and Liu 1998; Plyasunov, O'Connell, and Wood 2000; Plyasunov *et al.* 2000; Sedlbauer, O'Connell, and Wood 2000; Plyasunov *et al.* 2001; Plyasunov, Shock, and O'Connell 2006). In recent years extensions have been made to ionic liquid systems and to solubilities of solids, such as pharmaceuticals, in mixed solvents (Abildskov, Ellegaard, and O'Connell 2009; Ellegaard, Abildskov, and O'Connell 2009; Abildskov, Ellegaard, and O'Connell 2010a, 2010b; Ellegaard 2011).

The purpose of this chapter is to review these applications of FST methodology for correlating and predicting properties of a wide variety of systems and as a basis for validating equation of state models. Some of the material is already in the previous review monograph (O'Connell 1990), though little of that discussion is repeated here. Since that time, advances have been made in several directions; these are the present focus. Section 9.2 describes applications to pure component and mixture densities, Section 9.3 treats phase equilibria with a focus on dilute solutions, and Section 9.4 describes the use of FST formulations to test EOS models and mixing rules against data for binary TCFIs and DCFIs.

9.2 FST Modeling of Pure Component and Mixture Density Dependences on Pressure and Composition

Relations of the integrals of total correlation functions (TCFI) to derivatives for the variations of molar density to pressure can be written for systems of any number of components, as in Section 1.1.6. These involve matrix inverses with all of the pair TCFIs of the system. Section 1.2 gives the full relations for applications to pure, binary and ternary systems. As shown in Section 1.2.3, there is also a set of relations for the derivatives in terms of the DCFI which are somewhat simpler and more direct. There are two modeling objectives with these relations. One is to obtain a solution density at elevated pressures; the other is to obtain the component partial molar volumes for the solution density variations with composition. The next section describes approaches that have been used for both objectives in a wide variety of pure and binary systems.

9.2.1 Compressibilities

FST gives relations for the reduced bulk modulus and the partial molar volume of component i to integrals of the total and direct correlation functions (TCFIs and DCFIs) (Section 1.2). The greatest use of this relationship has been for compressed liquids where the TCFI and DCFI show simple corresponding states dependence on density with weak temperature dependence (Brelvi and O'Connell 1972, 1975b, 1975a; Mathias and O'Connell 1979; Mathias and O'Connell 1981; Campanella, Mathias, and O'Connell 1987; Huang and O'Connell 1987; Abildskov, Ellegaard, and O'Connell 2010a). In terms of DCFIs, the expression is,

$$\left(\frac{\partial \beta p}{\partial \rho} \right)_{T, \{x\}} = \sum_{i=1}^{n_c} x_i \sum_{j=1}^{n_c} x_j [1 - C_{ij}(T, \{ \rho \})] \quad 9.1$$

The general expression for TCFIs involves matrix inverses. For pure components, Equation 9.1

becomes Equation 1.65 of Section 1.3.1, which is simple for TCFIs,

$$1/\rho\kappa_T k_B T = 1 - C = 1/(1 + \rho G) \quad 9.2$$

Following the initial approach of Brelvi (Brelvi and O'Connell 1972) for $(1 - C)$, the most comprehensive corresponding states correlation was by Huang (Huang and O'Connell 1987) where C , scaled by a characteristic parameter C^* , is correlated by polynomials in ρ , scaled by V^* , and T , scaled by T^* ,

$$C = C^* \sum_{i=0}^3 \sum_{j=0}^2 a_{ij} (\rho V^*)^i (\tau)^j \quad 9.3$$

where $\tau = T/T^*$, which is always less than unity. The parameters C^* , V^* , and T^* are given for many substances by Huang (Huang and O'Connell 1987) and Poling, *et al.* (Poling, Praunitz, and O'Connell 2000) as well as for ionic liquids by Abildskov, *et al.* (Abildskov, Ellegaard, and O'Connell 2010a). The correlation has been applied to mixtures by employing mixing rules for V^* and T^* . An atomic group contribution method was also established (Huang and O'Connell 1987). Figure 9.1 shows the behavior of the scaled DCFI. Note that there is essentially no temperature dependence of C/C^* when ρV^* is less than 1.0, about 2.5 times the critical density. Close inspection shows there is a crossover of the isotherms near $\rho V^* = 0.93$ (Huang and O'Connell 1987).

[Inert Figure 9.1]

An alternative corresponding states model for DCFI formulates a perturbation about hard spheres, with an added term linear in density. This approach has been used successfully for organic substances (Mathias and O'Connell 1981; Campanella, Mathias, and O'Connell 1987) and also for ionic liquids (Abildskov, Ellegaard, and O'Connell 2010a),

$$1 - C_{ij} = (1 - C_{ij}^{hs}) + \rho \left\{ 2V_{ij}^* \tilde{b}(T / T_{ij}^*) - \left[V_{ii}^* \tilde{b}^{hs}(T / T_{ii}^*) + V_{jj}^* \tilde{b}^{hs}(T / T_{jj}^*) \right] \right\} \quad 9.4$$

The reduced covolumes, \tilde{b} and \tilde{b}^{hs} , are generalized functions of reduced temperature and multiplied by a characteristic volume, V^* . Expressions for the hard-sphere DCFI of Equation 9.4 are given by Mathias (O’Connell 1981) and Campanella, *et al.* (Campanella, Mathias, and O’Connell 1987). Abildskov, *et al.* (Abildskov, Ellegaard, and O’Connell 2010a) give the most recent correlations for the hard-sphere diameters and linear-density coefficients as functions of reduced temperature. Ionic liquid characteristic parameters for Equations 9.3 and 9.4 are listed in along with group contribution characteristics for ILs (Abildskov, Ellegaard, and O’Connell 2010a).

Comparisons of these correlations with experiment are given in the next section. “Experimental” compressibilities are typically values manipulated from densities measured at discrete pressures, so direct comparisons of densities of compressed fluids are more reliable than compressibilities.

9.2.2 Pure component and solution densities

The pressure dependence of liquid densities can be obtained by isothermal integration of Equation 9.1 over a change in density from a reference state, ρ^0 , p^0 , T , and $\{x\}$, such as ambient or saturated, to the desired state, p , T , and $\{x\}$. In terms of the DCFIs, for which most applications have been made,

$$\frac{p(T, \rho, \{x\}) - p(T, \rho^0, \{x\})}{k_B T} = \int_{x_i \rho^0}^{x_i p} \sum_{i=1}^{n_c} x_i \frac{\bar{V}_i}{k_B T \kappa_T} d\rho_i = \int_{x_i \rho^0}^{x_i p} \sum_{i=1}^{n_c} x_i \left(\sum_{j=1}^{n_c} x_j [1 - C_{ij}(T, \rho_i)] \right) \Big|_{T, \{x\}} d\rho_i \quad 9.5$$

A general integration procedure for these relations is described by O’Connell (O’Connell 1981;

O'Connell 1994; O'Connell 1995), though for models of the forms 9.3 and 9.4, analytic relations exist. The equations below are given by Abildskov, *et al.* (Abildskov, Ellegaard, and O'Connell 2009).

For Equation 9.3, the pressure difference can be solved iteratively to obtain ρ ,

$$\frac{p(T, \rho) - p^0(T, \rho^0)}{RT} = \left[1 - C * b_1(\tilde{T}) \right] (\rho - \rho^0) - C * \left[b_2(\tilde{T}) V * \frac{\rho^2 - (\rho^0)^2}{2} + b_3(\tilde{T}) V *^2 \frac{\rho^3 - (\rho^0)^3}{3} + b_4(\tilde{T}) V *^3 \frac{\rho^4 - (\rho^0)^4}{4} \right] \quad 9.6$$

where the coefficients $b_i(\tilde{T})$ are combinations of those in Equation 9.3 and are listed by Abildskov, *et al.* (Abildskov, Ellegaard, and O'Connell 2009). It should be noted that predictions of pressure/density differences, such as done here, are much more accurate than those that attempt to obtain high-pressure densities directly, since errors in estimation of the reference density, ρ^0 , a quantity that is normally easy to measure, are eliminated.

A worked example of this correlation is described in Section 4-12 of (Poling, Praunitz, and O'Connell 2000). Parameters for many substances are given by O'Connell (O'Connell 1990; O'Connell 1995) and Huang (Huang and O'Connell 1987). For densities greater than twice the critical density, the accuracy is extremely good for a wide variety of substances.

Figure 9.2 shows pressures computed at measured densities at different temperatures for the ionic liquid $[C_1C_2Im][Tf_2N]$ using the correlation of Equation 9.6 (Abildskov, Ellegaard, and O'Connell 2010a). The agreement is normally better than comparable methods (Paduszynski and Domanska 2012). Figure 9.2 shows that the measurements by different workers (Gardas *et*

al. 2007; Jacquemin *et al.* 2007) are different for both the reference densities and compressibilities, since the low pressure intercepts and the slopes of the lines are not the same. While the correlation cannot distinguish which reference density might be correct, the lines associated with the calculations suggest that the compression data of Gardas, *et al.* (Gardas *et al.* 2007) may be more reliable at lower temperatures, though they are between the slopes from the data at higher T .

[Insert Figure 9.2]

The relations based on Equation 9.4 from (Abildskov, Ellegaard, and O'Connell 2010a) are,

$$\frac{p - p^0}{k_B T} = \left(\frac{p^{hs}}{k_B T} \right) - \left(\frac{p^{hs}}{k_B T} \right)^0 + \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} (x_j x_i \rho^2 - x_i^0 x_j^0 \rho^{02}) (b_{ij} - b_{ij}^{hs}) \quad 9.7$$

For pure components, this becomes,

$$\frac{p - p^0}{k_B T} = \left(\frac{p^{hs}}{k_B T} \right) - \left(\frac{p^{hs}}{k_B T} \right)^0 + (\rho^2 - \rho^{02}) (b_{ii} - b_{ii}^{hs}) \quad 9.8$$

where the *hs* expressions are given below. The elements of the $n_c \times n_c$ matrix \mathbf{b} are calculated using,

$$b_{ij} = \tilde{b}_{ij} V_{ij}^* \quad 9.9$$

with,

$$\tilde{b}_{ij} = c_1 + \frac{c_2}{\tilde{T}_{ij}} + \frac{c_3}{\tilde{T}_{ij}^2} + \frac{c_4}{\tilde{T}_{ij}^3} + \frac{c_5}{\tilde{T}_{ij}^8} \quad 9.10$$

and the set of $\{c\}$ values is,

$$c^T = \{0.3625065 \quad -0.7140666 \quad -1.7543882 \quad 0.47075 \quad -0.0041793\} \quad 9.11$$

The characteristic V_{ij}^* of Equation 9.9 is,

$$V_{ij}^* = \frac{(\sqrt[3]{V_i^*} + \sqrt[3]{V_j^*})^3}{8} \quad 9.12$$

while the characteristic \tilde{T}_{ii} for Equation 9.10 when $i \neq j$ is,

$$\tilde{T}_{ij} = \frac{T}{(1-k_{ij})\sqrt{T_{ii}^* T_{jj}^*}} \quad 9.13$$

The hard-sphere terms are,

$$\left(\frac{p^{hs}}{RT}\right) = \frac{6}{\pi} \left(\frac{\xi_0}{1-\xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{(\xi_2)^3(3-\xi_3)}{(1-\xi_3)^3} \right) \quad 9.14$$

The hard-sphere quantities are,

$$\begin{aligned} \xi_q &= \frac{\pi}{6} \sum_{j=1}^{n_c} \rho_j \sigma_j^q = \frac{\pi}{6} \rho \sum_{j=1}^{n_c} x_j \sigma_j^q & ; & \quad q = 0, 1, 2, 3 \\ \xi_q^0 &= \frac{\pi}{6} \sum_{j=1}^{n_c} \rho_j^0 \sigma_j^q = \frac{\pi}{6} \rho^0 \sum_{j=1}^{n_c} x_j^0 \sigma_j^q & ; & \quad q = 0, 1, 2, 3 \end{aligned} \quad 9.15$$

where,

$$\sigma_i = \sqrt[3]{\frac{3}{2\pi} b_{ii}^{hs}} \quad 9.16$$

For a pure component, 9.14 becomes,

$$\left(\frac{p^{hs}}{RT}\right) = \frac{6}{\pi} \left(\frac{\xi}{1-\xi} + \frac{3\xi}{(1-\xi)^2} + \frac{(\xi)^2(3-\xi)}{(1-\xi)^3} \right) \quad 9.17$$

and Equation 9.15 plus Equation 9.16 give,

$$\xi = \frac{1}{2} b_{ii}^{hs} \quad 9.18$$

The elements of the $n_c \times n_c$ matrix \mathbf{b}^{hs} in Equation 9.7 are calculated with the following

equations,

$$b_{ij}^{hs} = \frac{b_{ii}^{hs} + b_{jj}^{hs}}{2} \quad 9.19$$

$$b_{ii}^{hs} = V_i^* \tilde{b}_{ii}^{hs}, \quad \tilde{b}_{ii}^{hs} = \begin{cases} \frac{\alpha_1}{\tilde{T}_i^{\alpha_2}} & \tilde{T}_i = \frac{T}{T_i^*} > 0.73 \\ \beta_1 e^{\beta_2 \tilde{T}_i} & \tilde{T}_i = \frac{T}{T_i^*} < 0.73 \end{cases} \quad 9.20$$

where the sets of constants $\{\alpha\}$ and $\{\beta\}$ are,

$$\alpha = \begin{Bmatrix} 0.65386227 \\ 0.16067976 \end{Bmatrix}, \quad \beta = \begin{Bmatrix} 0.807662393 \\ -0.22010926 \end{Bmatrix} \quad 9.21$$

Though the forms of all the other equations are the same, the values used in Equation 9.11 and 9.21 by Mathias and O'Connell (Mathias and O'Connell 1981) and Campanella, *et al.* (Campanella, Mathias, and O'Connell 1987) differ somewhat from those developed by Abildskov, *et al.* (Abildskov, Ellegaard, and O'Connell 2009) and Ellegaard, *et al.* (Ellegaard, Abildskov, and O'Connell 2011) which were revised to more successfully correlate the properties of ionic liquids. Those given here are from Campanella (Campanella, Mathias, and O'Connell 1987). As in Equation 9.6, the pressure difference is analytic in reduced density and temperature, providing a solution for ρ at a specified p or for p at a specified ρ .

9.2.3 Partial Molar Volumes

There is a direct FST connection of partial molar volumes of components in solution to DCFI,

$$\left(\frac{\partial \beta p V}{\partial N_i} \right)_{T,V,N_{j \neq i}} = \frac{\bar{V}_i}{k_B T \kappa_T} = \sum_{j=1}^{n_c} x_j [1 - C_{ij}(T, \{\rho\})] \quad 9.22$$

This relation has a number of aspects that lead to successful correlations, including in the near-

critical region where \bar{V}_i^∞ may diverge (O'Connell 1994; O'Connell and Liu 1998; Plyasunov, O'Connell, and Wood 2000; Plyasunov *et al.* 2000; Sedlbauer, O'Connell, and Wood 2000; Plyasunov *et al.* 2001; Plyasunov, Shock, and O'Connell 2006). It also gives a correction about a misinterpretation of the pressure dependence of gas solubility (Mathias and O'Connell 1979; Mathias and O'Connell 1981; O'Connell 1981), and notes errors in the values of partial molar volumes of gases from supercritical fluid chromatography (Liu and O'Connell 1998). The practical range of dilute solution compositions where a property is independent of the component's concentration, or is effectively at infinite dilution, depends on the property and the desired accuracy. Composition sensitivity is greater for activity coefficients than for partial molar volumes and enthalpies. This section describes several aspects of partial molar volume modeling, focusing on infinitely dilute solutions and the near-critical region.

9.2.3.1 Partial Molar Volumes at Infinite Dilution

For dilute solutions, the volume of a dilute binary solution might be approximated as,

$$V_m(T, p, x_1) \approx (1 - x_2)\bar{V}_1^o + x_2\bar{V}_2^\infty \quad x_2 < 0.1 \quad 9.23$$

Under this assumption, Equation 9.22 for a binary becomes,

$$\lim_{N_2 \rightarrow 0} \left(\frac{\partial \beta p V}{\partial N_2} \right)_{T, V, N_1} = \frac{\bar{V}_2^\infty}{k_B T \kappa_{T,1}^o} \equiv A_{Kr} = 1 - C_{12}^\infty(T, \rho_1^o) \quad 9.24$$

The ratio of properties in 9.24 is called the Krichevskii function, A_{Kr} , and identified at the solvent critical point as the Krichevskii parameter (Levelt Sengers 1991). The first FST correlation for partial molar volumes of gases in liquids was done by Brelvi (Brelvi and O'Connell 1975c), using characteristic properties for his correlation of the reduced bulk modulus (Brelvi and O'Connell 1972). Recent work (Ellegaard, Abildskov, and O'Connell 2011) has used the form

of Equation 9.4 for partial molar volumes of gases in ILs. The comparisons with data for these systems seem not to be as successful as for their compressibilities and phase equilibria, for reasons that are not apparent.

For systems far from the critical point of component 1, the value of \bar{V}_2^∞ is relatively small and positive. However, Cooney and O'Connell (Cooney and O'Connell 1987) noted that the variation with pressure of \bar{V}_i^∞ for aqueous salts, even at conditions approaching the critical where \bar{V}_2^∞ is negative, could be successfully correlated with water density and requiring temperature dependence only below 100 °C. This was followed by recognizing from data as well as theory, that A_{Kr} for aqueous nonelectrolytes is well-behaved from ambient conditions through the critical region, even though as $T \rightarrow T_{c1}$, \bar{V}_2^∞ diverges strongly (Levelt Sengers 1991). Typically, if $T_{c1} > T_{c2}$, such as for volatile nonelectrolytes (Hnědkovský, Majer, and Wood 1995), $\bar{V}_2^\infty \rightarrow \infty$, while for $T_{c1} < T_{c2}$, such as for inorganics (Hnědkovský, Wood, and Majer 1996) and salts (Sedlbauer, O'Connell, and Wood 2000), $\bar{V}_2^\infty \rightarrow -\infty$. The heat capacity at infinite dilution, \bar{C}_p^∞ , also diverges for all systems (see Figure 9.8 below). However, since A_{Kr} is only very weakly divergent (Levelt Sengers 1991), $1 - C_{12}^\infty$ is well-behaved over essentially all experimentally accessible conditions. In fact, data over wide ranges of density show that A_{Kr} , like pure component DCFI, is virtually independent of temperature for both nonelectrolytes and electrolytes (O'Connell 1995; O'Connell, Sharygin, and Wood 1996). For example, Figure 9.3 shows the variation of A_{Kr} from experiment for several small solutes in water for wide ranges of temperature and density along with the correlation,

$$A_{Kr} = 1 + a_1\rho + a_2[\exp(c\rho) - 1] \quad 9.25$$

where a_1 and a_2 are solute-dependent parameters and c is a universal constant (O'Connell, Sharygin, and Wood 1996).

[Insert Figure 9.3]

Further investigations have shown the generality of this behavior. Both Plyasunov (Plyasunov *et al.* 2001; Plyasunov 2011) and Majer, *et al.* (Majer, Sedlbauer, and Bergin 2008) have studied volumetric and phase behavior of many aqueous systems and developed group contribution methods for a large variety of nonelectrolytes in water at extreme conditions. This behavior has led to extensive models for thermodynamic properties and phase behavior of dilute aqueous systems (Plyasunov, O'Connell, and Wood 2000; Plyasunov *et al.* 2000; Sedlbauer, O'Connell, and Wood 2000; Plyasunov *et al.* 2001; Plyasunov, Shock, and O'Connell 2006; Majer, Sedlbauer, and Bergin 2008; Plyasunov 2011). Details of these models are described below.

9.2.4 Partial molar volumes at finite concentrations

One issue associated with the above systems is defining the mole fraction of solute where infinite dilution is no longer a satisfactory assumption. Liu (Liu and O'Connell 1998; O'Connell and Liu 1998) investigated this in the context of supercritical chromatography measurements for partial molar volumes. Expanding the DCFI in solute mole fraction about infinite dilution shows that first-order terms can be significant even at mole fractions of the order of 10^{-3} . This suggests that common conditions and literature treatments of data could be unreliable. The analysis was extended to solubilities in supercritical fluids, noting that at least one set of data did not display the required thermodynamic consistency for phase equilibria and volumetric behavior.

9.3 FST Modeling of Phase Equilibria Involving Dilute Solutions

Issues in dilute solution modeling have been discussed extensively (Cabezas and O'Connell 1993). The application of FST to these systems provides a powerful method for both solution nonidealities and densities as shown in the above sections, by integrating the FST partial derivatives of chemical potential from a reference state to a solution state. The most successful cases have been for solutions with strong nonidealities such as for supercritical gas components (Mathias and O'Connell 1981; Campanella, Mathias, and O'Connell 1987; O'Connell and Liu 1998; Plyasunov, O'Connell, and Wood 2000; Plyasunov *et al.* 2000; Sedlbauer, O'Connell, and Wood 2000; Plyasunov *et al.* 2001; Plyasunov, Shock, and O'Connell 2006) and for solids in liquids (Ellegaard, Abildskov, and O'Connell 2009; Abildskov, Ellegaard, and O'Connell 2010a, 2010b; Ellegaard 2011). Also, FST formulations give the basis for correlations used for supercritical extraction of solids into near-critical solvents (Liu and O'Connell 1998; O'Connell and Liu 1998). The usual form is done with fugacities rather than chemical potentials since complexities of the latter at infinite dilution are eliminated (see Section 1.1.4).

9.3.1 Models based on activity coefficients

The thermodynamic formulation of the fugacities in a binary appropriate for dilute solutions is,

$$\begin{aligned} f_1 &= (1 - x_2) \gamma_1 f_1^0 \\ f_2 &= x_2 \gamma_2^* H_{21} \end{aligned} \tag{9.26}$$

where $\lim_{x_1 \rightarrow 1} \gamma_1 = 1$ and $\lim_{x_1 \rightarrow 1} \gamma_2^* = 1$ and H_{21} is Henry's constant or the fugacity of the hypothetical pure component 2 in a state consistent with linear mole fraction dependence at infinite dilution,

and f_1^0 is the fugacity of pure component 1 in its standard state. The property γ_2^* is the activity coefficient, related to the excess chemical potential, in the “unsymmetric convention” (Prausnitz, Lichtenthaler, and Gomes de Azevedo 1999). See below for dealing with mixed solvents.

Kirkwood and Buff (Kirkwood and Buff 1951) included expressions for γ_2^* in single solvents from a Taylor’s series expansion in solute mole fraction. The coefficients were collections of infinite-dilution (pure component 2) pair KBIs at the first order and pair and triplet KBIs at the second order. The form used for applications is,

$$\ln \gamma_2^* = \Delta_{12}^0 (-2x_2 + x_2^2) + \Delta_{112}^0 x_2^3 + \dots \quad 9.27$$

The Gibbs-Duhem Equation gives,

$$\ln \gamma_1 = \Delta_{12}^0 x_2^2 + \dots \quad 9.28$$

O’Connell (O’Connell 1971a) also gave these formulae in terms of direct correlation function integrals with,

$$\Delta_{12}^0 = \frac{1}{2} \left[(1 - C_{11}^0) - \frac{(1 - C_{12}^0)^2}{(1 - C_{22}^0)} \right] \quad 9.29$$

and an equivalent for Δ_{112}^0 in terms of pair and triplet DCFI. Expressions were also given for the partial molar volumes and the reduced bulk modulus to lowest order of the expansion in mole fraction. It is expected that this correlation, with an empirical value of Δ_{12}^0 , would be adequate up to solute mole fractions of $x_2 \sim 0.1$. Brelvi (Brelvi and O’Connell 1975c) developed a correlation for Δ_{12}^0 in the spirit of his prior work (Brelvi and O’Connell 1972).

If models for TCFIs or DCFIs are available, the complete expression for both $\ln \gamma_1$ and $\ln \gamma_2^*$ can

be obtained through appropriate integration. The expression is simpler for DCFIs,

$$\ln \gamma_i^* = \sum_{j=1}^{n_c} \int_{x_j^0 \rho^0}^{x_j \rho} \frac{[1 - C_{ij}(T, \rho_i)]}{\rho} d\rho_j \quad 9.30$$

If the solution state is specified by pressure rather than density, the same model for DCFI is used in both Equations 9.5 and 9.30 to obtain ρ and γ_1^* for a specified state of T , p , and $\{x\}$ relative to the state T , p^0 , ρ^0 , and $\{x^0\}$ where γ_2^* is unity. The methodology for this approach is fully described by O'Connell (O'Connell 1981; O'Connell 1994; O'Connell 1995).

This method was used for gas solubility and solution densities of liquids by Mathias and O'Connell (Mathias and O'Connell 1979; O'Connell 1981) and expanded by Campanella, *et al.* (Campanella, Mathias, and O'Connell 1987) for a wide variety of systems including hydrocarbons, organics, and aqueous solvents. The method has recently been extended by Ellegaard *et al.* (Ellegaard, Abildskov, and O'Connell 2009) and Abildskov *et al.* (Abildskov, Ellegaard, and O'Connell 2010b) for use in IL systems. For a model of the form of Equation 9.4, this becomes,

$$\ln \gamma_i(T, \rho, \{x\}; \rho^0, \{x^0\}) = \ln \gamma_i^{hs}(T, \rho, \{x\}; \rho^0, \{x^0\}) + 2 \sum_{j=1}^{n_c} (x_j \rho - x_j^0 \rho^0) (b_{ij} - b_{ij}^{hs}) \quad 9.31$$

where,

$$\begin{aligned}
\ln \gamma_i^{hs}(T, \rho, \{x\}; \rho^0, \{x\}^0) = & \\
& \left[\ln \rho - [\ln(1 - \xi_3)] \left[1 - \left(\frac{\xi_2 \sigma_i}{\xi_3} \right)^2 \left(3 - 2 \frac{\xi_2 \sigma_i}{\xi_3} \right) \right] \right. \\
& \left. + \frac{3(\xi_2 \sigma_i + \xi_1 \sigma_i^2) - (\xi_2 \sigma_i)^3 (2 - \xi_3) / \xi_3^2}{1 - \xi_3} + \frac{3}{\xi_3} \left(\frac{\xi_2 \sigma_i}{1 - \xi_3} \right)^2 + \frac{\pi}{6} \sigma_i^3 \frac{p^{hs}}{RT} \right] \\
& - \left[\ln \rho^0 - [\ln(1 - \xi_3^0)] \left[1 - \left(\frac{\xi_2^0 \sigma_i}{\xi_3^0} \right)^2 \left(3 - 2 \frac{\xi_2^0 \sigma_i}{\xi_3^0} \right) \right] \right. \\
& \left. + \frac{3(\xi_2^0 \sigma_i + \xi_1^0 \sigma_i^2) - (\xi_2^0 \sigma_i)^3 (2 - \xi_3^0) / (\xi_3^0)^2}{1 - \xi_3^0} + \frac{3}{\xi_3^0} \left(\frac{\xi_2^0 \sigma_i}{1 - \xi_3^0} \right)^2 + \frac{\pi}{6} \sigma_i^3 \left(\frac{p^{hs}}{RT} \right)^0 \right]
\end{aligned} \quad 9.32$$

There are two aspects of this treatment that are significant. First, one or more binary constants are used in models such as Equation 9.4, *e.g.*, in Equation 9.13. Therefore, when Equation 9.46 (?) is taken to the limit of pure solvent 3, there is a relation between the Henry's Constants,

$$\lim_{x_3 \rightarrow 1} \ln \gamma_2^* = \ln \left(\frac{H_{2R}}{H_{23}} \right) = \int_{\rho_{pure R}}^0 \frac{[1 - C_{2R}(T, \{\rho\})]}{\rho} d\rho_R + \int_0^{\rho_{pure 3}} \frac{[1 - C_{23}(T, \{\rho\})]}{\rho} d\rho_3 \quad 9.33$$

Therefore, if the binary constant, k_{2R} is set or determined from experiment, Equation 9.33 determines k_{23} . Second, this also means that one can predict solute solubility in a solvent i from that in a convenient reference solvent, R ,

$$\begin{aligned}
f_i &= (1 - x_2) \gamma_i f_i^0 \\
f_2 &= x_2 \gamma_2^+ H_{2R}
\end{aligned} \quad 9.34$$

with,

$$\lim_{x_R \rightarrow 1} \ln \gamma_2^+ = 1 \quad 9.35$$

Here,

$$\ln \gamma_2^+ = \int_{\rho_{pure R}}^{x_R \rho} \frac{[1 - C_{2R}(T, \{\rho\})]}{\rho} d\rho_R + \int_0^{x_3 \rho} \frac{[1 - C_{23}(T, \{\rho\})]}{\rho} d\rho_3 \quad 9.36$$

Examples of using this with good success for hydrogen in different solvents, including for model coal liquids, based on a single reference solvent are given by Campanella, *et al.* (Campanella, Mathias, and O'Connell 1987) and O'Connell (O'Connell 1995). Treatment of complex mixed solvents, including for actual coal liquids, is also described in those references. This concept also works quite well for ILs (Abildskov, Ellegaard, and O'Connell 2009; Ellegaard, Abildskov, and O'Connell 2010).

Figure 9.4 shows predictions of pressure versus liquid mole fraction for the methane (1) and m-cresol system where the Henry's Constant of Equation 9.26 was obtained from fitting data directly (solid lines) or predicted with quinolone (dashed lines) as the reference solvent in Equation 9.34. As the arrows show, the prediction is not uniformly accurate in this case. Better results have been obtained with other solutes, especially hydrogen, nitrogen, and carbon monoxide, including mixed solvents, as shown by Campanella, *et al.* (Campanella, Mathias, and O'Connell 1987). Figures 9.5 and 9.6 show similar results for a system containing hydrogen and an ionic liquid (Abildskov, Ellegaard, and O'Connell 2009).

[Insert Figure 9.4, 9.5 and 9.6]

9.3.2 Models based on equations of state

For infinitely dilute solutions, the temperature independence of A_{Kr} at higher densities leads to the Henry's Constant of Equation 9.26 by integrating Equation 9.24. The relations are,

$$\ln \left(\frac{\beta \phi_2^\infty p}{\rho_1^o} \right) = \int_0^{\rho_1^o} (A_{Kr} - 1) \frac{d\rho}{\rho} \quad 9.37$$

From this relation, a formulation can be made in terms of the infinite dilution properties of

hydration for water as the solvent, such as the difference of Gibbs energies between the fluid at the designated reference pressure, p^0 , and the infinitely dilute solute at p ,

$$\Delta_h G_2^\infty(T, p) = RT \left[\ln \frac{\Phi_2^\infty p}{p^0} \right] \quad 9.38$$

This yields Henry's constants via,

$$H_{21}(T, p) = \exp \left[-\Delta_h G_2^\infty(T, p) / RT \right] \quad 9.39$$

Standard thermodynamic manipulations yield the infinite dilution enthalpy, entropy, and isobaric heat capacity of hydration (Plyasunov, O'Connell, and Wood 2000; Sedlbauer, O'Connell, and Wood 2000). For example,

$$\Delta_h C_{p,2}^\infty = -T^2 \left(\frac{d^2 \Delta_h G_2^\infty / T}{dT^2} \right) \quad 9.40$$

The issues are how to utilize known solution information at low temperatures and pressures that do depend on T and to express the properties at conditions below the critical temperature where there is temperature dependence of A_{Kr} . This approach need not be limited to aqueous systems, but those are the only ones which have been treated.

The first approach (Plyasunov, O'Connell, and Wood 2000) was to augment the high density function of Equation 9.25 with temperature-dependent correlations of cross (B_{12}) and pure solvent (B_{11}) second virial coefficients to include the low density behavior for the integral of Equation 9.37. An analytically integrable form was adopted:

$$\begin{aligned} A_{Kr} = & (1 - \alpha_1) + \alpha_1 \left[(1 - C_{11}^0) \right] + 2\rho \{ B_{12}(T) - B_{11}(T) \} \exp(k_1 \rho) \\ & + \rho \left(\frac{\alpha_2}{T^5} + \alpha_3 \right) \left[\exp(k_2 \rho) - 1 \right] \end{aligned} \quad 9.41$$

where values of B_{11} and B_{12} are obtained from the square-well potential model, k_1 and k_2 are

universal constants, and α_1 , α_2 , and α_3 are solute-dependent parameters. The full final relations of Equations 9.37 to 9.40 are given by Plyasunov, *et al.* (Plyasunov *et al.* 2000). These have been used to obtain infinite dilution thermodynamic properties of many organic substances in water (Plyasunov *et al.* 2001; Plyasunov, Shock, and O'Connell 2006). Figure 9.7 shows results for H₂S in water at various pressures and temperatures.

[Insert Figure 9.7]

The alternative route to aqueous solute properties based on FST was to use a finite pressure reference state where properties could be obtained and compute the difference in Gibbs energy between the desired state and the reference state (Sedlbauer, O'Connell, and Wood 2000). This allows calculations for electrolytes which would not have second virial coefficients that could be used at low densities as in Equation 9.41. The relation here for A_{Kr} is similar to Equation 9.41,

$$A_{Kr} = (1 - \beta_1) + \beta_1 \left[(1 - C_{11}^0) \right] + \rho \left\{ \beta_2 + \beta_3 \exp(1500/T) + \beta_4 \exp(c_1 \rho) + \delta \left[\exp(c_2 \rho) - 1 \right] \right\} \quad 9.42$$

where values of c_1 and c_2 are universal constants and β_1 , β_2 , β_3 , and β_4 are solute-dependent parameters. The value of δ has a specific value for the class of solute: cation, anion, nonelectrolyte.

Again, analytic expressions for $\Delta_h \bar{G}_2^\infty$ and H_{21} are found using Equations 9.37 to 9.39 (Sedlbauer, O'Connell, and Wood 2000), though slightly differently than by Plyasunov, *et al.* (Plyasunov, O'Connell, and Wood 2000; Plyasunov *et al.* 2000). The modification to deal with temperatures below the critical is to add a temperature-dependent correction term to the heat

capacity, which is different for nonelectrolytes and electrolytes,

$$\Delta_h \bar{C}_{p,2}^{\infty corr} = \beta_5 \frac{(T - T_c)^2}{(T - 228)} \quad T < T_{c1} \quad \text{Aqueous nonelectrolytes} \quad 9.43$$

$$= 0 \quad T \geq T_{c1}$$

$$\Delta_h \bar{C}_{p,2}^{\infty corr} = (T - T_c) \left[\frac{\beta_5}{(T - 228)} + \beta_6 \right] \quad T < T_{c1} \quad \text{Aqueous electrolytes} \quad 9.44$$

$$= 0 \quad T \geq T_{c1}$$

These analytically integrable expressions are included in the evaluations for $\Delta_h \bar{G}_2^{\infty}$ and for H_{21} (Sedlbauer, O'Connell, and Wood 2000). Figure 9.8 shows results for this model for aqueous NaCl with data for infinite dilution partial molar volumes and heat capacities at elevated temperatures. Results for Henry's Constants are also quite accurate.

[Insert Figure 9.8]

9.3.3 Solubilities in Mixed Liquid Solvents

While the above treatments are for solutes in single solvents, many applications of interest involve mixed solvents, especially for gases and pharmaceutical compounds. FST has been used to develop successful descriptions of such systems. Chapter 10 describes the approach of Shulgin and Ruckenstein. The focus here is on “excess solubility”, $\ln x^{ex}$, the difference in solubility in a real solvent mixture and that for the solvents as an ideal solution (Prausnitz, Lichtenthaler, and Gomes de Azevedo 1999). For very dilute solutions, the solubility is the reciprocal of the Henry's constant, so typically the “excess Henry's Constant”, H_2^{Ex} , is modeled,

$$\ln H_2^{Ex} \equiv \ln H_{2m} - \sum_i^{n_s} x_i \ln H_{2i} \quad 9.45$$

where the sum is over all solvents. Most measurements and models have been for binary solvents where the variation of H_2^{Ex} can be positive or negative or both. Empirical models have been developed, especially because the variation of H_2^{Ex} with composition is similar for all solutes and is mostly determined by the substances of the solvent mixture. FST approaches have been among the most successful for both gaseous and solid solutes in mixed solvents as also described in Chapter 10.

9.3.3.1 Gas Solubility in Mixed Solvents

There have been two FST approaches to gas solubility in mixed solvents. The first (O'Connell 1971a) expressed H_2^{Ex} in terms of collections of DCFI with simple parameterization; details of the relations are given in Section 9.3.3.2. The second (Mathias and O'Connell 1979; Campanella, Mathias, and O'Connell 1987) used the DCFI model of Equation 9.4 by integrating the DCFI for the solute from one pure solvent, identified as reference solvent, R , to the mixture composition, which for a binary is given by x_R . Then,

$$H_2^{Ex} \equiv (1 - x_R) \ln(H_{2R} / H_{23}) + \ln \gamma_2^* \quad 9.46$$

where $\ln \gamma_2^*$ is found from Equation 9.30 with ρ^0 being the pure reference solvent density, and the solution component densities being those for the mixed solvent, $\rho_i = x_i \rho_m$ for $i = R, 3$. For most systems, the mixture density used can be that for an ideal solution, though for aqueous systems, the excess volume is large enough that it must be taken into account (Campanella, Mathias, and O'Connell 1987; O'Connell 1995). Figure 9.9 shows results for H_2^{Ex} of ethylene in aqueous acetone and aqueous methanol. The complex behavior of the alcohol system is captured

reasonably well, and quantitative agreement for the acetone system is obtained only if the solution excess volume is included. Without this contribution, the results are similar to those of the simplest model where H_2^{Ex} is set equal to the negative of the excess Gibbs energy of the solvent mixture (O'Connell and Prausnitz 1964). It should be noted that the method was applied to the solubility of ethane and ethylene in the ternary solvent water, methanol, and acetone with good success when the solvent excess volumes were estimated by binary additivity.

[Insert Figure 9.9]

9.3.3.2 Solid Solubility in Mixed Solvents

The dissolution of solids into liquids is often a dilute solution situation and, as for gases, FST modeling following the approach of O'Connell (O'Connell 1971a) has been applied (Ellegaard, Abildskov, and O'Connell 2009; Ellegaard, Abildskov, and O'Connell 2010). If the solid is pure and the solution is ideal, the solubility can be found from the properties of the pure solute. This is given in (Ellegaard, Abildskov, and O'Connell 2010) as,

$$\ln x_2^{id} = -\frac{\Delta h_{m2}}{R} \left(\frac{1}{T} - \frac{1}{T_{m2}} \right) + \frac{\Delta C_{pm2}}{R} \left[\ln \left(\frac{T}{T_{m2}} \right) - 1 + \frac{T_{m2}}{T} \right] \quad 9.47$$

where T_{m2} is the melting temperature, Δh_{m2} is the enthalpy of melting, and ΔC_{pm2} is the difference in heat capacity of the hypothetical subcooled liquid and the solid from T_{m2} to T .

For mixed solvent systems, it is common to define an excess solubility,

$$x_2^{Ex} \equiv \ln x_2 - x_1 \ln x_{2,1} - (1 - x_1) \ln x_{2,3} \quad 9.48$$

in the limit,

$$\lim_{x_2 \rightarrow 0} x_2^{Ex} = -H_2^{Ex} \quad 9.49$$

For estimations of dilute solid solubility, an expansion similar to Equation 9.27 is done for a ternary system and to the first order,

$$H_2^{Ex} = \lim_{x_2 \rightarrow 0} \frac{x_3}{2} \left(\frac{\partial \ln \gamma_3}{\partial x_3} \right)_{T,P,N_1,N_2} + \frac{x_1}{2} \left(\frac{\Delta_{12}^m}{1 + x_1 x_3 \Delta_{13}^m} - \Delta_{12}^0 \right) + \frac{x_3}{2} \left(\frac{\Delta_{23}^m}{1 + x_1 x_3 \Delta_{13}^m} - \Delta_{23}^0 \right) \quad 9.50$$

where ^m indicates the solvent mixture and ⁰ indicates pure solvent. With suitable approximations (O'Connell 1971a; Ellegaard, Abildskov, and O'Connell 2009; Ellegaard, Abildskov, and O'Connell 2010), in particular that $\Delta_{li}^m = \Delta_{li}^0$, the final form becomes,

$$H_2^{Ex} = \lim_{x_2 \rightarrow 0} \frac{x_3}{2} \left(\frac{\partial \ln \gamma_3}{\partial x_3} \right)_{T,P,N_1,N_2} \left(1 + x_1 \Delta_{12}^0 + x_3 \Delta_{23}^0 \right) \quad 9.51$$

The partial derivative is obtained from parameters found by regressing vapor-liquid equilibrium data for the solvent mixture. The estimated solubilities are not very sensitive to these parameters. There are multiple ways to obtain the Δ_{li}^0 values. One is to use data from solute solubilities in the pure solvents and regress the parameters Δ_{12}^0 and Δ_{23}^0 separately.

Then,

$$\Delta_{2i}^0 = 2 \frac{\ln x_{2i}^{id} - \ln x_{2i}}{(1 - x_{2i})^2} \quad 9.52$$

This method requires values of the pure solute properties. Alternatively, if solute solubilities in mixed solvents are available, these data can be regressed for the parameters simultaneously and the pure solute properties are not needed. Note that the theory demands that parameters for a particular solute-solvent pair be the same for all systems involving the pair, regardless of the additional solvent. In (Ellegaard, Abildskov, and O'Connell 2010), those regressed from ternary

data were assumed independent of temperature, though the obtained binary values did vary with T .

In (Ellegaard, Abildskov, and O'Connell 2010), data were analyzed from 9 pharmaceutical solutes in a total of 68 binary mixtures of 10 solvents, with some of the mixtures at different temperatures. The absolute average relative deviation of using parameters from binary data was 23% while that from correlation of ternary data was 11%. Additional study of this method is described in (Ellegaard 2011) with more solutes and binary solvents, as well as in some ternary solvents. Figure 9.10 shows excess solubility results for representative systems.

[Insert Figure 9.10]

9.4 FST Properties of Reactive Components and Strong Electrolyte Solutions

The FST statistical mechanics described above are for nonelectrolyte systems. The treatment of solutions of ionizing salts, or in fact any system where speciation of the input components occurs, requires additional analysis. This section describes some elements of this area; other aspects are discussed in Chapter 8.

There are two general situations in which the particles in a solution do not have the same identity as those that are put into the system: when a component dissociates and when components can combine to form other species. The first case is commonly identified with salts forming ions with electrostatic charges. In both cases, the reactions need not be complete, so that the solution can have the original species (components) as well as the new species. Further, the speciation

need not lead to detectable entities. Thus, the “chemical theory of solutions” and the “solution of groups” descriptions of solution nonideality (Prausnitz, Lichtenthaler, and Gomes de Azevedo 1999) involve virtual species considered to have thermodynamic properties. The general thermodynamics of such systems was established by Perry, *et al.* (Perry, Telotte, and O’Connell 1981) and their FST analysis was later articulated (Perry and O’Connell 1984).

The concept is that all species considered to have thermodynamic properties will also have pair correlation functions. However, because of stoichiometry, there are constraints on both the properties and the correlation function integrals. Further, though the collection of charges on ions requires electroneutrality only as a consequence of the stoichiometry, there are long-range electrostatic correlations of the ions that affect FST modeling of electrolytes. This aspect has also been treated (Cabezas and O’Connell 1986; Perry, Cabezas, and O’Connell 1988; O’Connell 1993). The purpose of this section is to briefly outline the basis and results available.

9.4.1 FST of Reactive Components

The principal effect of speciation is the expansion of the composition space associated with the input components to the larger composition space of the species. The goal is to express with models the properties of the species in the larger space and then project these properties into the smaller component space that has the proper number of independent variables and properties, *i.e.*, the number of components plus 2, to obtain measurable properties. The key mathematical entity is the projection operator, \mathbf{W} , a nonsquare ($n \times n_c$) matrix accounting for the stoichiometric connection between the n_c components and the n species. The full development, mathematical details and specific examples are given by Perry (Perry, Telotte, and O’Connell 1981; Perry and

O'Connell 1984). Applications to strong electrolytes are given by Perry, *et al.* (Perry, Cabezas, and O'Connell 1988), O'Connell (O'Connell 1993; O'Connell, Hu, and Marshall 1999), as discussed in the next section. We provide here a simple example.

A traditional thermodynamics approach to reactions uses the set of the initial moles of species, $\{n_i^0\}$, the matrix ($n \times R$) of reaction stoichiometric coefficients, ν , and the set of extents of the R independent reactions, ξ , to obtain the moles of species at some point in the reaction,

$$\{n_i\} = \{n_i^0\} + \nu^T \{\xi\} \quad 9.53$$

An example is the reaction $A_1 + A_2 = 2A_3$ where the components are 1 and 2 and the species are 1, 2 and 3. Equation 9.53 would give,

$$\begin{Bmatrix} n_1 \\ n_2 \\ n_3 \end{Bmatrix} = \begin{Bmatrix} n_1^0 \\ n_2^0 \\ n_3^0 \end{Bmatrix} + \begin{Bmatrix} -\xi \\ -\xi \\ 2\xi \end{Bmatrix} \quad 9.54$$

An approach that allows description of the independent thermodynamic properties of reacting systems uses a slight variation,

$$\{n\} = \mathbf{W} \{n_o\} \quad 9.55$$

where $\{n_o\}$ is the set of mole numbers of the input components. Then,

$$\mathbf{W} = \begin{bmatrix} 1 - \xi & 0 \\ -\xi & 1 \\ 2\xi & 0 \end{bmatrix} \quad 9.56$$

where the extent of reaction has been scaled to component 1. The importance of the latter form is that all independent partial molar properties can be related by,

$$\mathbf{W}^T \{\bar{X}\} = \{\bar{X}_o\} \quad 9.57$$

where X can be V, H, G , etc. In our example for partial molar volume,

$$\begin{Bmatrix} \bar{V}_1 \\ \bar{V}_2 \\ \bar{V}_3 \end{Bmatrix} = \begin{Bmatrix} \bar{V}_{1o} \\ \bar{V}_{2o} \\ \frac{1}{2}(\bar{V}_{1o} + \bar{V}_{2o}) \end{Bmatrix} \quad 9.58$$

Similar connections can be made for properties of mixing, excess properties, and activity coefficients. Using this approach on fluctuation properties is described by Perry and O'Connell (Perry and O'Connell 1984). The relations for TCFI among pairs of species are extremely complex with the extents of reactions embedded in the TCFI. However, those for DCFI are much more direct and the extents of reaction are contained in the projectors. Defining the desired matrix,

$$[A^{-1}]_{ij} = \left[\frac{\partial (\mu_{oi} / RT)}{\partial n_{oj}} \right]_{T,V,n_{ok} \neq j} \quad 9.59$$

The connection of the matrix of FST component derivatives, A^{-1} , to the matrix of species DCFI, C , is,

$$A^{-1} = K^T (x^{-1} - C) K \quad 9.60$$

where the elements of the matrix K are,

$$K_{ij} = W_{ij} + [v \xi' n_o]_{ij} \quad 9.61$$

And the elements of the matrix ξ' are,

$$[\xi']_{ij} = \left(\frac{\partial \xi_i}{\partial n_{oj}} \right)_{T,V,\mu_{ok} \neq j} \quad 9.62$$

Ultimately obtaining the desired properties such as density differences and activity coefficients would be complicated, but feasible. This seems not to have been attempted. A much simpler

case is for complete reactions, such as dissociation of strong electrolytes, is shown in the next section.

9.4.2 FST of Strong Electrolyte Solutions

Equations 9.60, 9.61, and 9.62 above can be used directly for FST properties of solutions with fully ionized salts (Perry and O'Connell 1984). In this case, the projection of the extent of reaction terms in Equation 9.62 are null and,

$$\mathbf{A}^{-1} = \mathbf{W}^T (\mathbf{x}^{-1} - \mathbf{C}) \mathbf{W} \quad 9.63$$

For dissociation of a salt $a_{v_a} b_{v_b}$ into ions, the FST derivatives are,

$$\begin{aligned} \left[\frac{\partial \beta \mu_{o1}}{\partial n_{o1}} \right]_{T,V,n_{o2}} &= x_1^{-1} - C_{11} \\ \left[\frac{\partial \beta \mu_{o1}}{\partial n_{o2}} \right]_{T,V,n_{o1}} &= -v_a C_{1a} = -v_b C_b = \left[\frac{\partial \beta \mu_{o2}}{\partial n_{o1}} \right]_{T,V,n_{o2}} \\ \left[\frac{\partial \beta \mu_{o2}}{\partial n_{o2}} \right]_{T,V,n_{o1}} &= \frac{v_a + v_b}{x_2} - \left[v_a^2 C_{aa} + 2v_a v_b C_{ab} + v_b^2 C_{bb} \right] \end{aligned} \quad 9.64$$

where $x_1 = N_{o1} / [N_{o1} + (v_a + v_b) N_{o2}]$ and $x_2 = 1 - x_1$. Models for the species DCFI can be used in Equations 9.64 to obtain solution thermodynamic properties in the same manner as was done with nonelectrolytes above.

However, examination of the Debye-Hückel limiting law (Perry, Cabezas, and O'Connell 1988) shows a major complication in that the long-range electrostatic interactions lead to divergences of the ion-ion correlation functions, c_{aa} , c_{ab} , and c_{bb} in the limit of infinite dilution. Analysis of the long-range contributions (Stell, Patey, and Høye 1981) leads to rigorous formulae for the

Limiting Law DCFIs, while more appropriate models for the Extended Limiting Law DCFIs are found (Perry, Cabezas, and O'Connell 1988; O'Connell 1993). The short-range contributions can be modeled by 2nd virial terms similar to those of Pitzer (Pitzer 1995); full expressions are given in (O'Connell, Hu, and Marshall 1999). The pressure and activity coefficient relations from Equations 9.5 and 9.30, are, respectively,

$$\begin{aligned} \frac{p - p^0}{k_B T} = & (\rho - \rho^0) - \left\{ \frac{1}{2} (\rho_{o1}^2 - \rho_{o1}^{02}) \Delta F_{11} + \rho_{o1} \rho_{o2} \Delta F_{12} + \rho_{o2}^2 \Delta F_{22} \right\} \\ & - \left\{ \frac{1}{3} (\rho_{o1}^3 - \rho_{o1}^{03}) \Delta \Phi_{111} + \rho_{o1}^2 \rho_{o2} \Delta \Phi_{112} + \rho_{o1} \rho_{o2}^2 \Delta \Phi_{112} + \rho_{o2}^3 \Delta \Phi_{222} \right\} \\ & + \rho_{o1} S_\gamma I^{3/2} \left\{ \frac{\partial \ln \epsilon}{\partial \rho_{o1}} \right\}_{T, \rho_{o2}=0} - c I^{3/2} - \frac{1}{3} S_\gamma I^{3/2} - S_\gamma \left\{ \frac{a}{b^3} \left[\frac{2}{9} (1 + b I^{1/2})^3 \right. \right. \\ & \left. \left. - \frac{1}{b^2} I + 2(1 + b I^{1/2}) - \frac{2}{3} \ln(1 + b I^{1/2}) - \frac{11}{9} \right] \right. \\ & \left. \left. + \frac{a}{3} I^{3/2} \ln(1 + b I^{1/2}) + \beta \alpha^2 I^2 \exp(-\alpha I^{1/2}) \right\} \end{aligned} \quad 9.65$$

$$\begin{aligned} \ln \gamma_2 = & \ln \left(\frac{\rho}{\rho^0} \right) - \frac{1}{v_2} \left\{ (\rho_{o1} - \rho_{o1}^0) \Delta F_{12} + \rho_{o1} \Delta F_{22} \right\} \\ & - \frac{1}{v_2} \left\{ \frac{1}{2} (\rho_{o1}^2 - \rho_{o1}^{02}) \Delta \Phi_{112} + \rho_{o1} \rho_{o2} \Delta \Phi_{122} + \rho_{o2}^2 \Delta \Phi_{222} \right\} - \frac{\omega}{v_2} S_\gamma I^{1/2} \\ & - \frac{\omega}{v_2} S_\gamma \left\{ a I^{1/2} \ln(1 + b I^{1/2}) + 2\beta \left[1 - \exp(-\alpha I^{1/2}) (1 + \alpha I^{1/2} - \alpha^2 / 2I) \right] \right\} \end{aligned} \quad 9.66$$

where I is the molar ionic strength and the Limiting Law Property, S_γ is,

$$S_\gamma = \left[\frac{2\pi e^6 N_A}{(\epsilon k T)^3} \right]^{\frac{1}{2}} \quad 9.67$$

The parameters are ΔF_{11} , ΔF_{12} , ΔF_{22} , $\Delta \Phi_{111}$, $\Delta \Phi_{112}$, $\Delta \Phi_{122}$, and $\Delta \Phi_{222}$. It was found (O'Connell, Hu, and Marshall 1999) that, except for ΔF_{22} and $\Delta \Phi_{222}$, these are ionically additive or follow simple combining rules. Using salt-specific parameters for ΔF_{22} and $\Delta \Phi_{222}$ gave excellent

agreement in densities and activity coefficients for fifteen 1-1, 1-2, and 2-1 salts over the entire range of data available. Figure 9.11 shows mean ionic activity coefficients and densities for the systems NaNO_3 and CaCl_2 . The sources of experimental information are given in Table 9.1.

The agreement is quite good up to high salt concentrations.

[Insert Figure 9.11 and Table 9.1]

Work has not continued on this approach because of the complexity of the expressions and the lack of ionic additivity, combined with only limited improvement in accuracy compared to other models with the same number of parameters. However, the tabulations of salt DCFI from evaluated data (Hu 1997) can provide tests for such other models.

9.5 Analysis of Equation of State Mixing and Combining Rules Using FST

The simplest fundamental connection between equations of state, expressed as Helmholtz functions of T , v , and $\{x\}$, and correlation function integrals is via the second composition derivative of the residual Helmholtz energy and DCFI,

$$1 - C_{ij} = N \left[\frac{\partial^2 \beta A^r}{\partial N_i \partial N_j} \right]_{T, V, N_k} \quad 9.68$$

As usual, the TCFI expressions are more complex because they involve matrix inverses of the second derivatives. Many applications use an EOS model that is cubic in molar volume, such as the generalized van der Waals form, with pure component parameters that depend upon composition according to mixing rules that employ combining rules with unlike interaction parameters of the solution components. An example is the original van der Waals EOS,

$$p = \frac{RT}{v - b(\{x\})} - \frac{a(\{x\})}{v^2} \quad 9.69$$

The Helmholtz energy, when written in the form for taking the derivatives of Equation 9.68 is,

$$\frac{A^r(T, V, \{N\})}{RT} = N \ln \left(\frac{N}{V - Nb(\{N\})} \right)^2 - \frac{N^2 a(\{N\})}{RTV} \quad 9.70$$

The derivatives can be taken for any set of mixing and combining rules. The well-known 1-fluid mixing rules are,

$$\begin{aligned} N^2 a(\{N\}) &= \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} N_i N_j a_{ij} \\ Nb(\{N\}) &= \frac{\sum_{i=1}^{n_c} \sum_{j=1}^{n_c} N_i N_j b_{ij}}{\sum_{i=1}^{n_c} N_i} \end{aligned} \quad 9.71$$

and, among the combining rule options, a common choice is,

$$\begin{aligned} a_{ij} &= (a_{ii} a_{jj})^{\frac{1}{2}} (1 - k_{ij}) \\ b_{ij} &= \frac{1}{2} (b_{ii} + b_{jj}) (1 - l_{ij}) \end{aligned} \quad 9.72$$

where k_{ij} and l_{ij} are binary parameters which are zero for pure components ($i = j$). For these choices, Equation 9.68 becomes,

$$1 - C_{ii} = \left(\frac{v}{v - b_{ii}} \right)^2 - \frac{2a_{ii}}{k_B T v} \quad 9.73$$

and,

$$1 - C_{ij} = 1 + \frac{(b_{ii} + b_{jj})(1 - l_{ij})}{v - b(\{x\})} + \frac{b_{ii} b_{jj}}{[v - b(\{x\})]^2} - \frac{2(a_{ii} a_{jj})^{\frac{1}{2}} (1 - k_{ij})}{k_B T v} \quad 9.74$$

Equation 9.74, and expressions from other EOS models can be used to test the accuracy of

mixing and combining rules by comparisons with experimental DCFI values. The EOS studied here is the Peng-Robinson (Peng and Robinson 1976) model,

$$\frac{p^{res}}{RT} = \frac{Nb(\{x\})}{V - Nb(\{x\})} - \frac{N^2a(T, \{x\}) / RT}{V^2 + 2Nb(\{x\})V + [Nb(\{x\})]^2} \quad 9.75$$

An initial effort in this direction was presented in by O'Connell and Clairmont (O'Connell and Clairmont 2010). The data bank of binary DCFI and TCFI values for a variety of subcritical systems given by Wooley and O'Connell (Wooley and O'Connell 1991) was used for DCFI comparisons as well as for composition variations of excess volume. The EOS models were the cubic original van der Waals and Peng-Robinson models, and the quintic DeSantis model, with mixing rules of the original van der Waals, Huron and Vidal, and Wong - Sandler forms (Poling, Praunitz, and O'Connell 2000). The last two rules use excess Gibbs energy results, usually from fitting VLE data, to establish mixture parameters that are more accurate for the composition dependence of liquid solutions. Figures 9.12 and 9.13 show DCFIs and V^E from this analysis for the binary CCl_4 (1) and methanol. The questions posed and conclusions were:

1. Do the EoS and mixing rules follow the composition variations for 1- C_{11} and 1- C_{22} from pure component to infinite dilution? The answer is sometimes, but not reliably.
2. Can binary parameters be found to describe the composition variations of 1- C_{12} and V^E ? The answer is generally yes, but not always.
3. Is there a difference in results for the van der Waals & G^E mixing rules? The answer is yes, but there is no preponderance of accuracy in one form or another. The van der Waals mixing rules, with 2 binary parameters, is quite satisfactory for nonassociating, nonsolvating systems. But no mixing rule is adequate for components with hydrogen

bonds in dilute solution. The accuracy of the descriptions of excess volume was uneven, with no apparent pattern of success or failure.

4. If experimental liquid volumes were used in the EOS to compute total pressures, the results were generally poor. The sensitivity of p to density is too great to obtain accurate values from the EOS.

[Insert Figure 9.12 and 9.13]

This work is far from complete because only a few of the systems in the data base were tested and no contemporary EOS models, such as SAFT (Muller and Gubbins 2001; Economou 2002), PC-SAFT (Gross and Sadowski 2001) and CPA (Kontogeorgis *et al.* 1996), which have been reviewed by Kontogeorgis and Folas (Kontogeorgis *et al.* 2006a, 2006b) and by Polishuk and Mulero (Polishuk and Mulero 2011), were examined.

9.6 Summary and Conclusions

It has been shown that models for DCFIs can lead to successful models for solution properties and phase equilibria, especially for strongly nonideal systems such as dilute solutions of gases and solids. Because FST formulations are for composition derivatives of pressure and chemical potential or fugacity, the evaluation can appear complex and requires property values at certain reference states. This may be the reason such models have not been implemented into process simulators. However, the reliability and accuracy of models based on perturbations from hard spheres, such as Equation 9.4, is quite good for very many systems, and the results can at least be used to generate local parameterizations and to validate EOS models. Ultimately, results from

molecular simulations, as described in Chapter 6, may lead to new relations for the thermodynamic models for use in process simulators.

Table 9.1 Sources of Data for Figure 9.11.

Salt	Property	Reference
NaNO ₃	Density	Janz, <i>et al.</i> 1970 Hamer and Wu 1972
	Activity	
	Coefficient	
CaCl ₂	Density	Romankiw and Chou 1983 Staples and Nuttall 1977
	Activity	
	Coefficient	

Figure 9.1 Scaled DCFI from Equation 9.3.

Figure 9.2 Density versus pressure for the IL $[\text{C}_1\text{C}_2\text{Im}][\text{TfN}]$. Data (■) from Gardas *et al.* (Gardas *et al.* 2007) and (♦) from Jacquemin, *et al.* (Jacquemin *et al.* 2007). Calculations of p using Equation 9.6 with p^0 , ρ^0 , and ρ from Jacquemin, *et al.* (Jacquemin *et al.* 2007) (—) and from Gardas, *et al.* (Gardas *et al.* 2007) (— —). The arrows identify the data associated with the lines. (Modified from J. Abildskov, M. D. Ellegaard, and J. P. O'Connell. 2010. Densities and isothermal compressibilities of ionic liquids - Modeling and application. *Fluid Phase Equilibria*. 295, 215.)

Figure 9.3 Variations of Krichevskii function, A_{Kr} , for various small solutes in water; (a) for high solvent densities, (b) for lower densities. Symbols for data, lines for Equation 9.25. (Reprinted with permission from J. P. O'Connell, A. V. Sharygin, and R. H. Wood. 1996. Infinite dilution partial molar volumes of aqueous solutes over wide ranges of conditions. *Industrial & Engineering Chemistry Research*. 35, 2808.)

Figure 9.4. Pressure versus liquid mole fraction for isotherms of methane with m-cresol. Symbols for data of Simnick, *et al.*, (Simnick *et al.* 1979a) (—) regression of temperature dependence of Henry's Constant in Equation 9.26, (---) prediction using Equation 9.34 with Henry's Constant for methane in quinoline fitted to data of Simnick, *et al.* (Simnick *et al.* 1979b). Arrows indicate prediction at $T = 462$ K is not accurate.

Figure 9.5. Pressure versus liquid mole fraction of hydrogen (1) in the IL [hmim][NTf2] calculated using Henry's Constant of Equation 9.26 fitted to data of Kumelan, *et al.* (Kumelan *et al.* 2006). —■ $T = 293.2\text{K}$; —● $T = 333.2\text{K}$; - - - ▲ $T = 373.2\text{K}$; · · · ♦ $T = 413.2\text{K}$. (Modified with permission from J. Abildskov, M. D. Ellegaard, and J. P. O'Connell. 2009. Correlation of phase equilibria and liquid densities for gases with ionic liquids. *Fluid Phase Equilibria*. 286, 95.)

Figure 9.6. Log ratio of fugacity to liquid mole fraction of hydrogen (1) in the IL [hmim][NTf2] calculated using Henry's Constant of Equation 9.26 fitted to data of Kumelan, *et al.* (Kumelan *et al.* 2006). —■ $T = 293.2\text{K}$; —● $T = 333.2\text{K}$; - - - ▲ $T = 373.2\text{K}$; · · · ♦ $T = 413.2\text{K}$. (Reprinted with permission from J. Abildskov, M. D. Ellegaard, and J. P. O'Connell. 2009. Correlation of phase equilibria and liquid densities for gases with ionic liquids. *Fluid Phase Equilibria*. 286, 95.)

Figure 9.7 Henry's Constants (H_{21}) for Hydrogen sulfide (2) in water (1) from Equations 9.37 to 9.41. (Reprinted with permission from A. Plyasunov, J. O'Connell, R. Wood, and E. Shock. 2000. Infinite dilution partial molar properties of aqueous solutions of nonelectrolytes. II. Equations for the standard thermodynamic functions of hydration of volatile nonelectrolytes over wide ranges of conditions including subcritical temperatures. *Geochimica Et Cosmochimica Acta*. 64, 2779.)

Figure 9.8 (Left) Infinite dilution partial molar volume of aqueous NaCl vs. water density at $p = 38$ MPa over $600 < T < 725$ K. (—) from Equation 9.42. (O) Extrapolations by Sedlbauer *et al.* (Sedlbauer, Yezdimer, and Wood 1998) of data of Majer *et al.* (Majer *et al.* 1991). (Right) Infinite dilution heat capacity of aqueous NaCl at $p = 28$ MPa over $640 < T < 680$ K. (—) from Equations 9.37 to 9.40 and 9.42 to 9.44. (O) Data of Carter (Carter 1992). (Reprinted with permission from J. Sedlbauer, J. O'Connell, and R. Wood. 2000. A new equation of state for correlation and prediction of standard molal thermodynamic properties of aqueous species at high temperatures and pressures. *Chemical Geology*. 163, 43.)

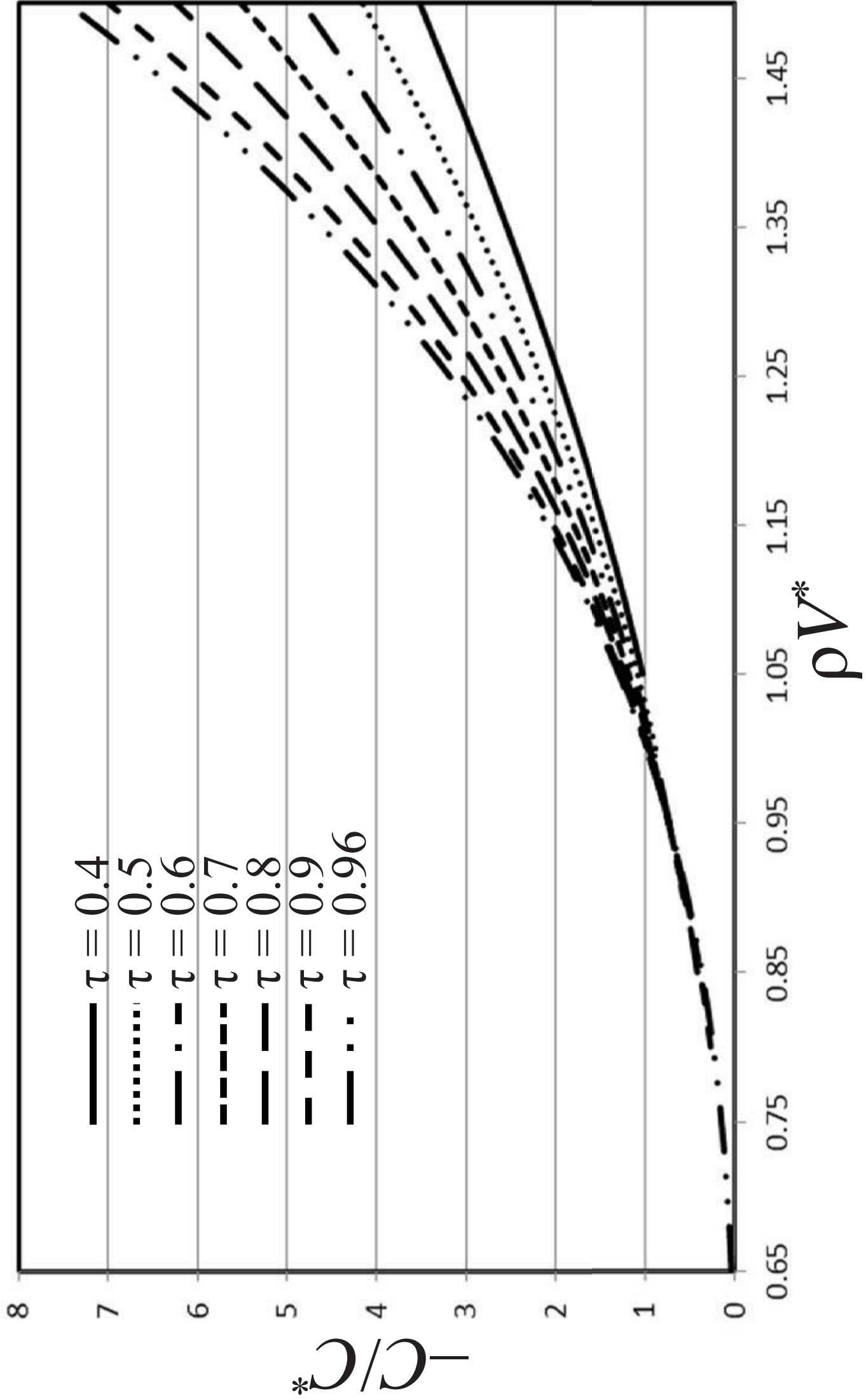
Figure 9.9 Excess Henry's Constants of Equation 9.46 for ethylene (2) in aqueous methanol and aqueous acetone solutions at 298.15 K. Data of Zeck and Knapp (Zeck and Knapp 1985), calculations with Equation 9.46 using experimental densities (—), zero excess volumes (- - -) and with an excess Gibbs energy rule (•••) (O'Connell and Prausnitz 1964).

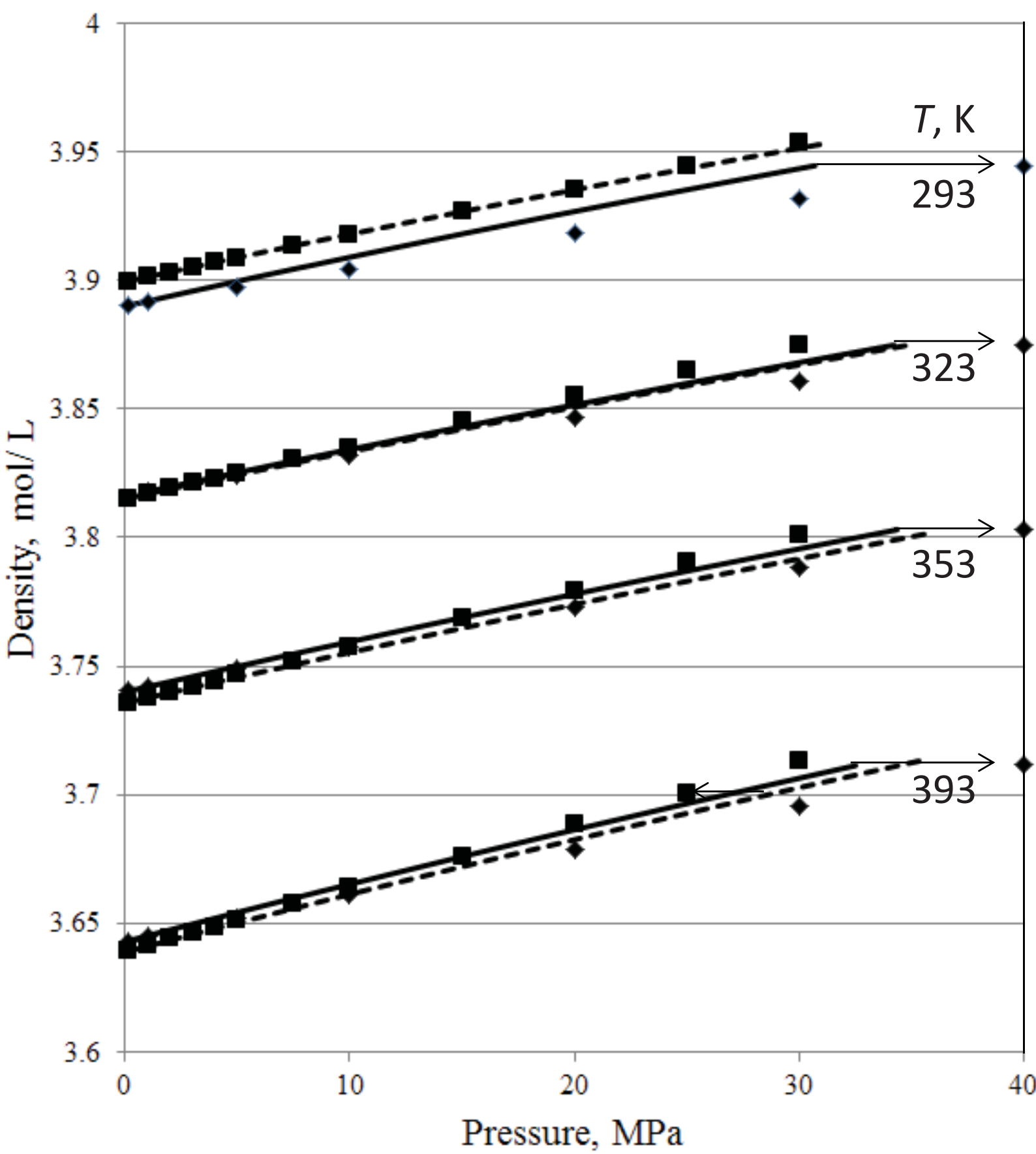
Figure 9.10 Estimated and experimental excess solubilities, x_2^{Ex} , of solid solutes in mixed solvents: Left: naphthalene (2) / water (1) / acetone (3), ♦ Data of J. M. Lepree, *et al.* (Lepree, Mulski, and Connors 1994). Right: β -carotene (2) / acetone (1) / n-hexane (3), ▲ Data of Treszczanowicz, *et al.* (Treszczanowicz *et al.* 2001); — Calculated.

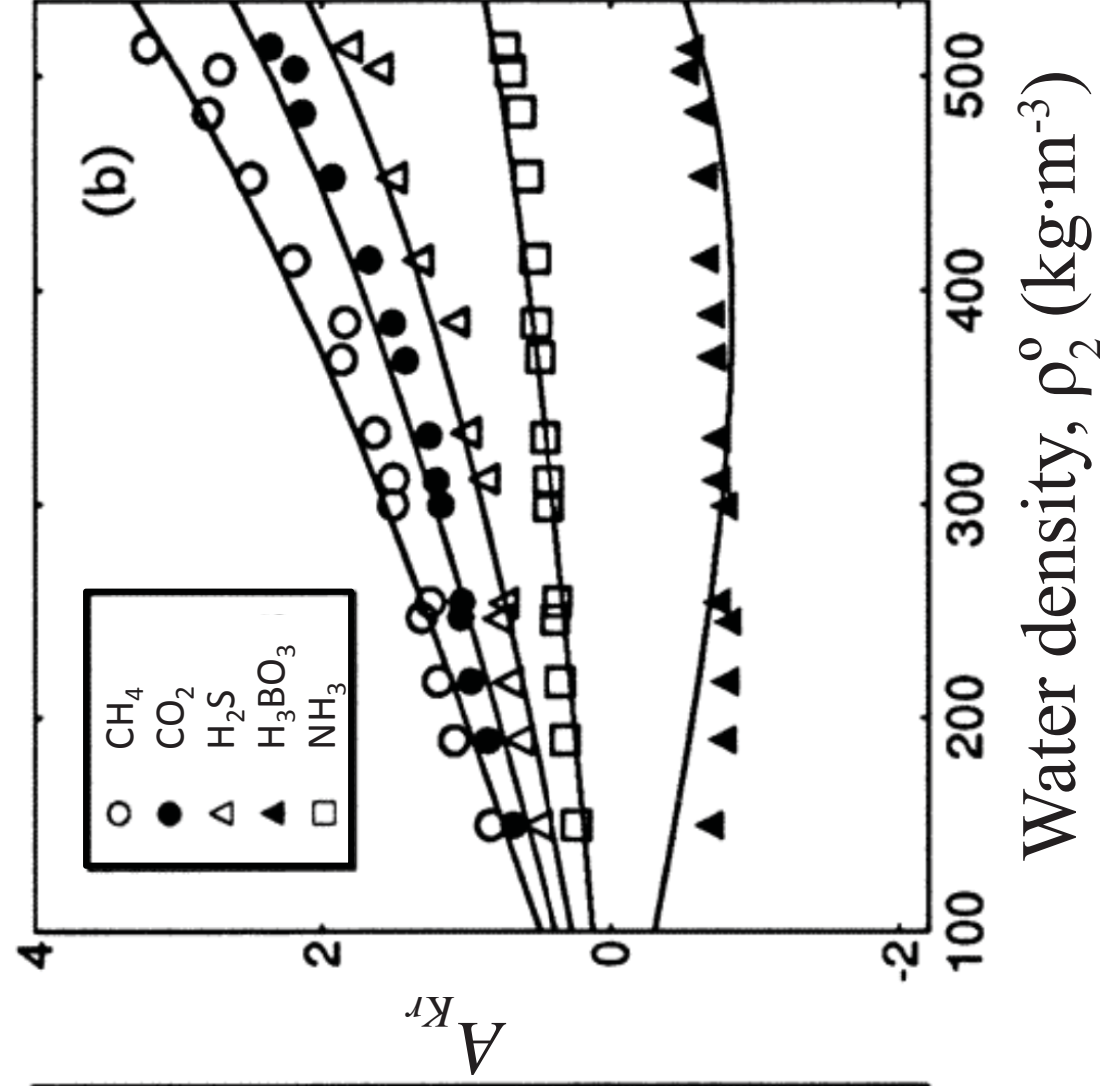
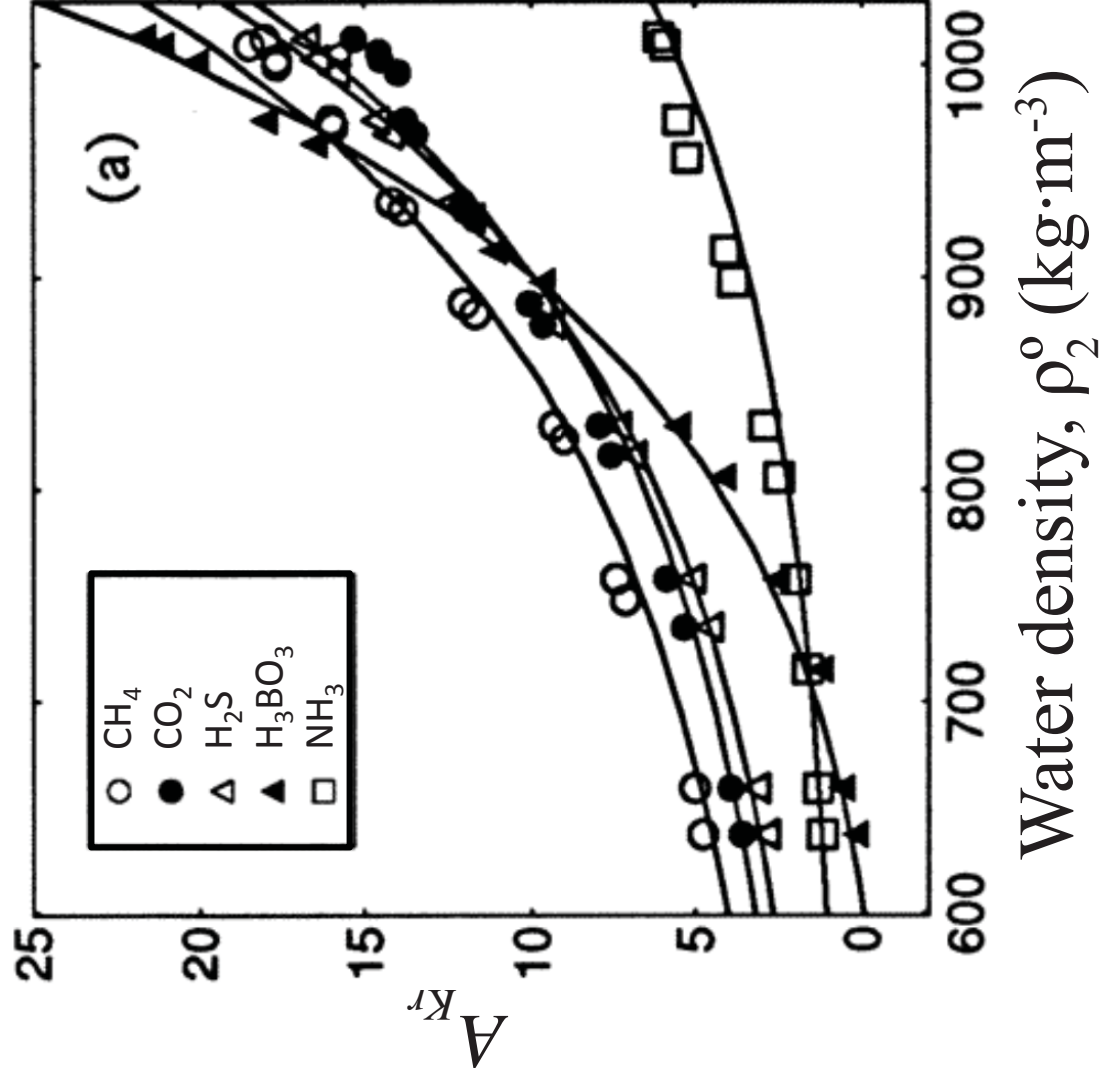
Figure 9.11 Densities and mean ionic activity coefficients for NaNO_3 (◆) and CaCl_2 (■) at 298.15 K. Data sources given in Table 9.1. Calculations (—) and (---) from Equations 9.65 to 9.67.

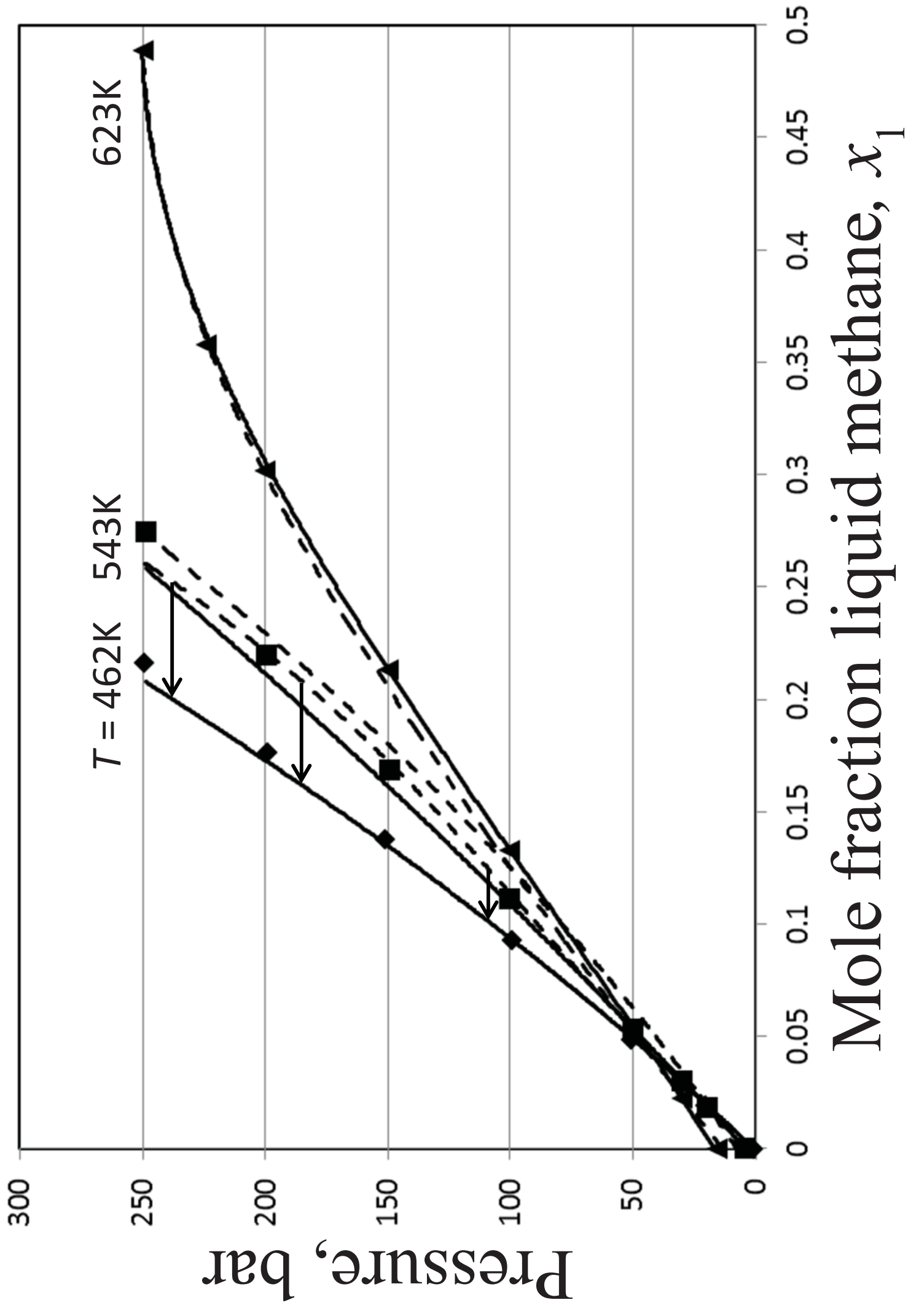
Figure 9.12 DCFIs for the CCl_4 – Methanol system at $T = 298.15$ K using Equation 9.74 with different mixing rules. EOS calculations from Peng-Robinson model, Equation 9.75, with the 2-parameter, 1-fluid, van der Waals mixing rule (- - -), Equation 9.74, and Wong-Sandler (Wong and Sandler 1992) G_m^E mixing rule (—). Data (■) from tabulations of Wooley and O’Connell (Wooley and O’Connell 1991).

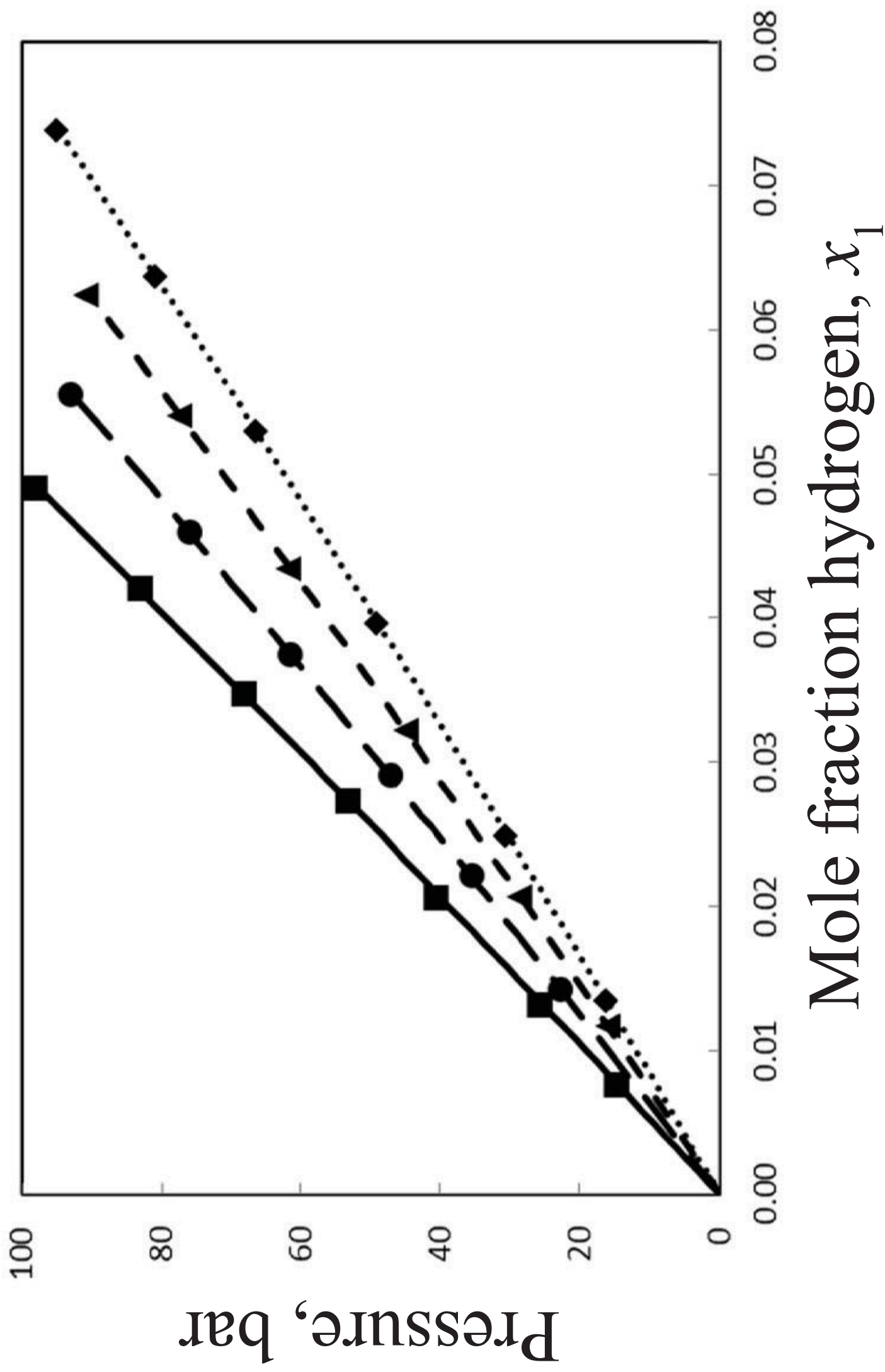
Figure 9.13 V_m^E for the CCl_4 – Methanol system at $T = 298.15$ K computed with different mixing rules. EOS calculations from Peng-Robinson model, Equation 9.75, with the 2-parameter, 1-fluid, van der Waals mixing rule (---) and Wong-Sandler (Wong and Sandler 1992) G^E mixing rule (—). Data (■) from tabulations of Wooley and O’Connell (Wooley and O’Connell 1991).

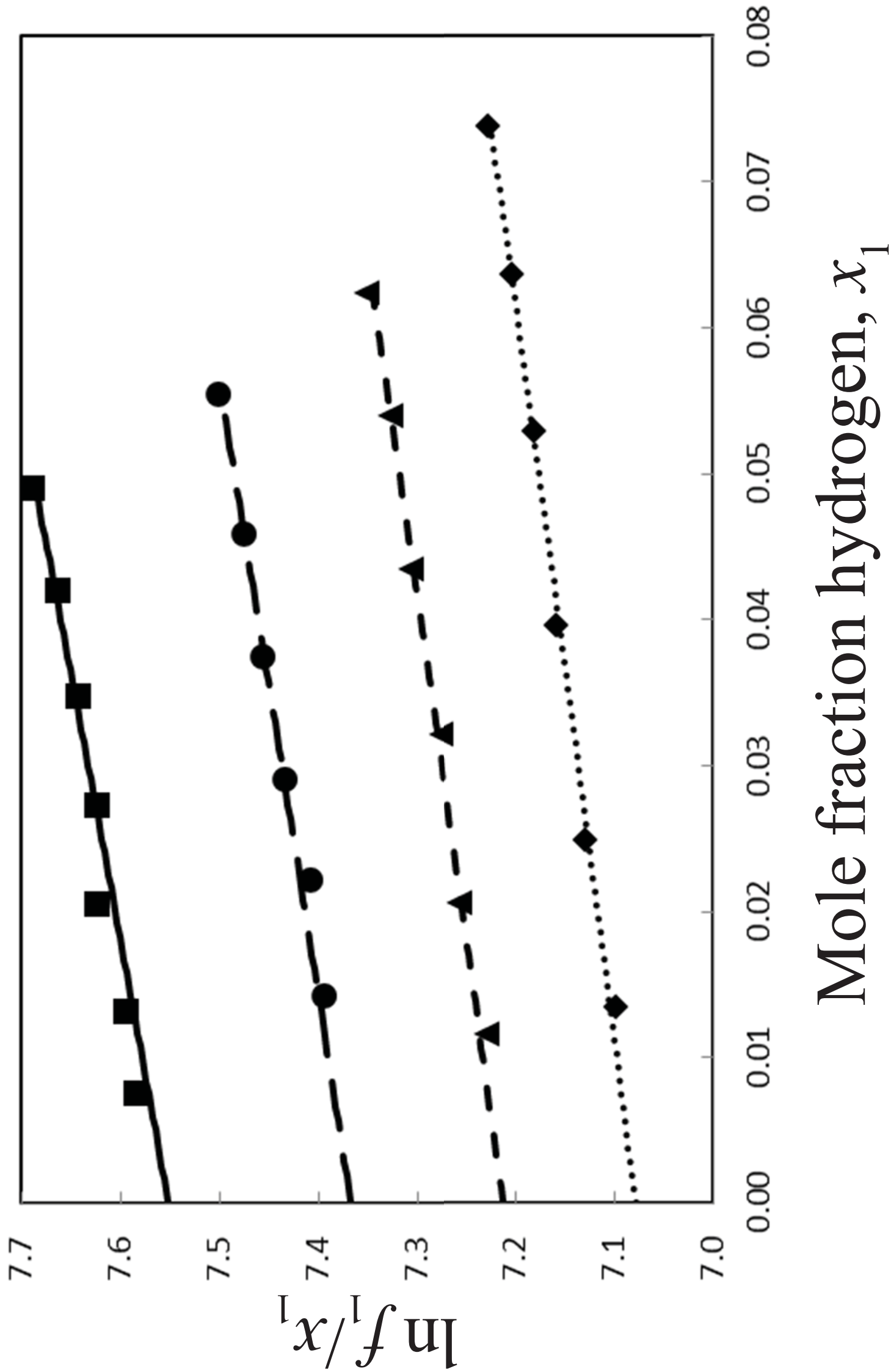


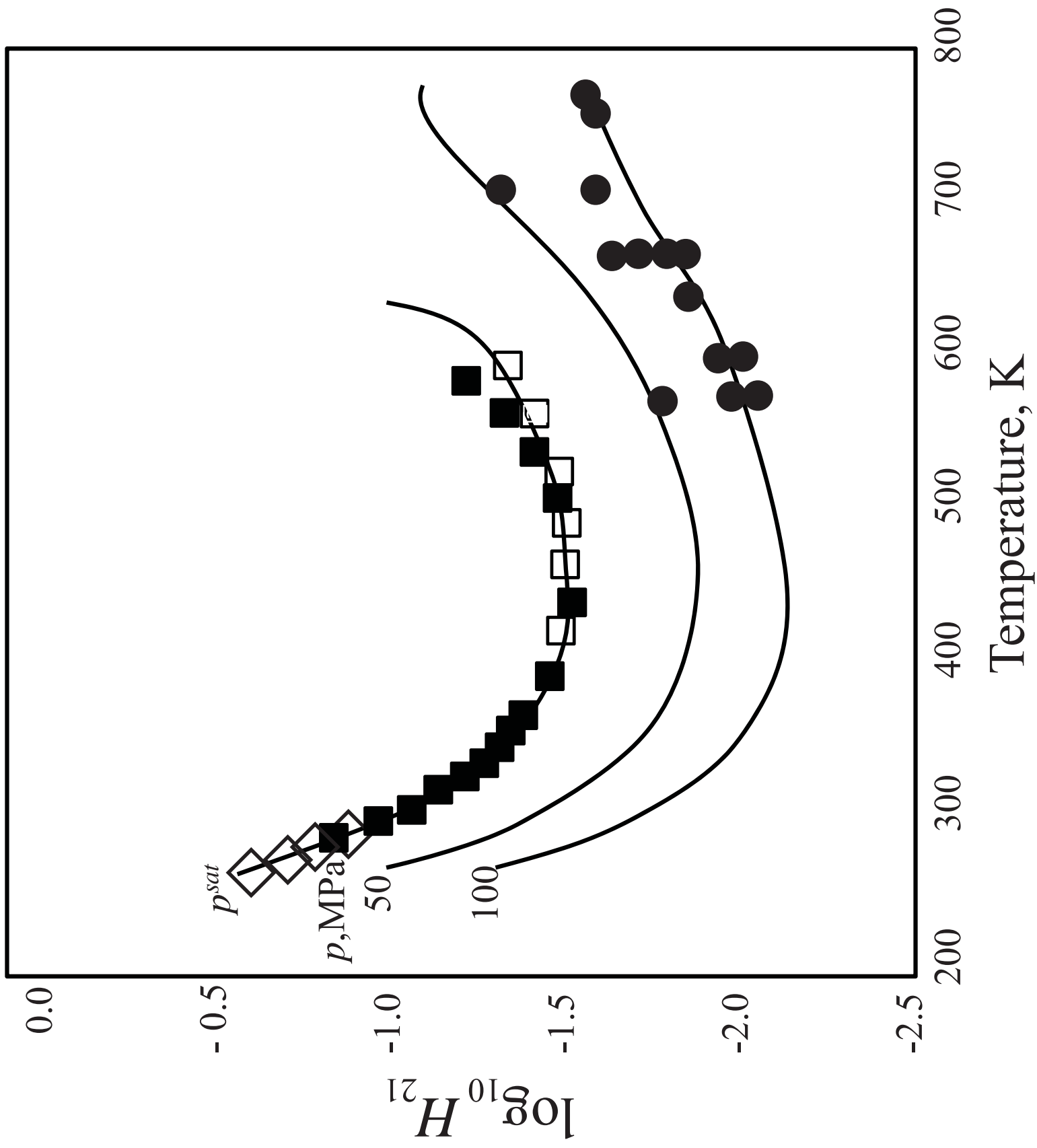


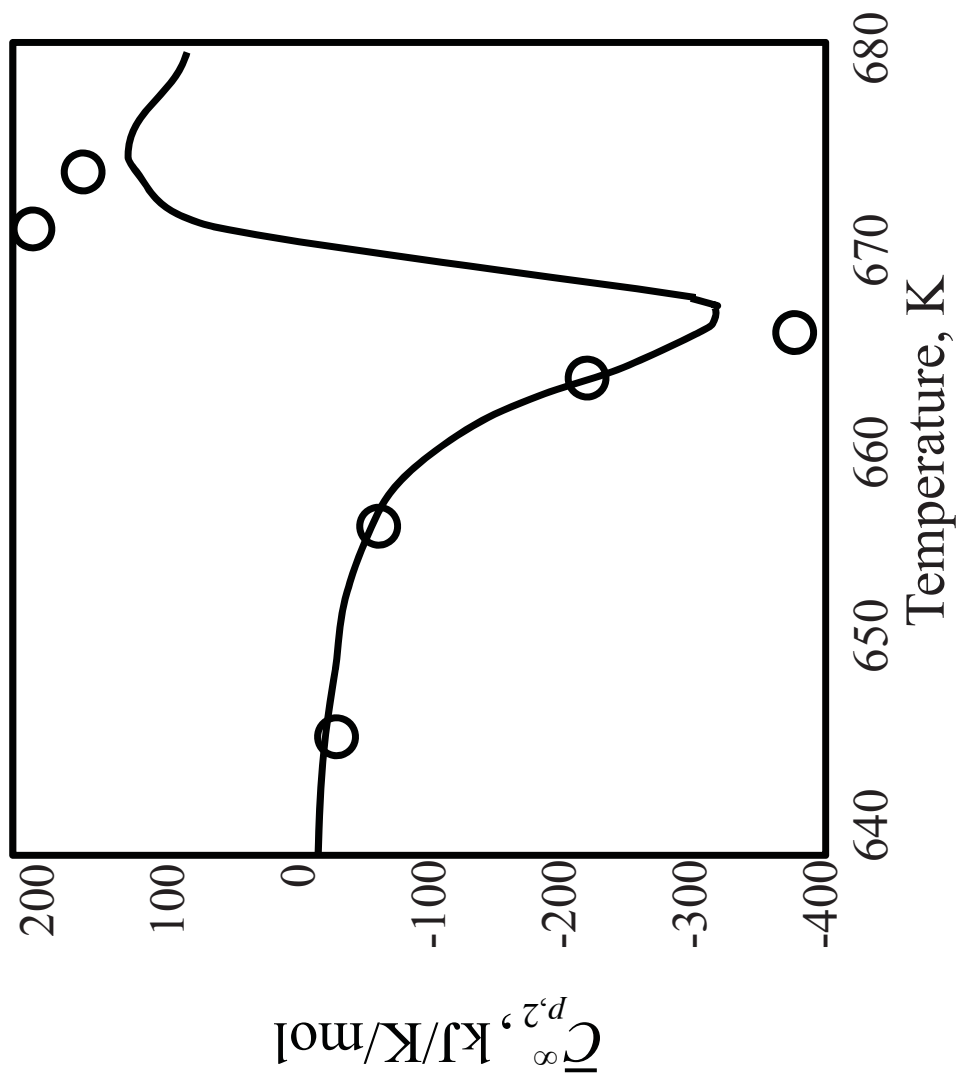
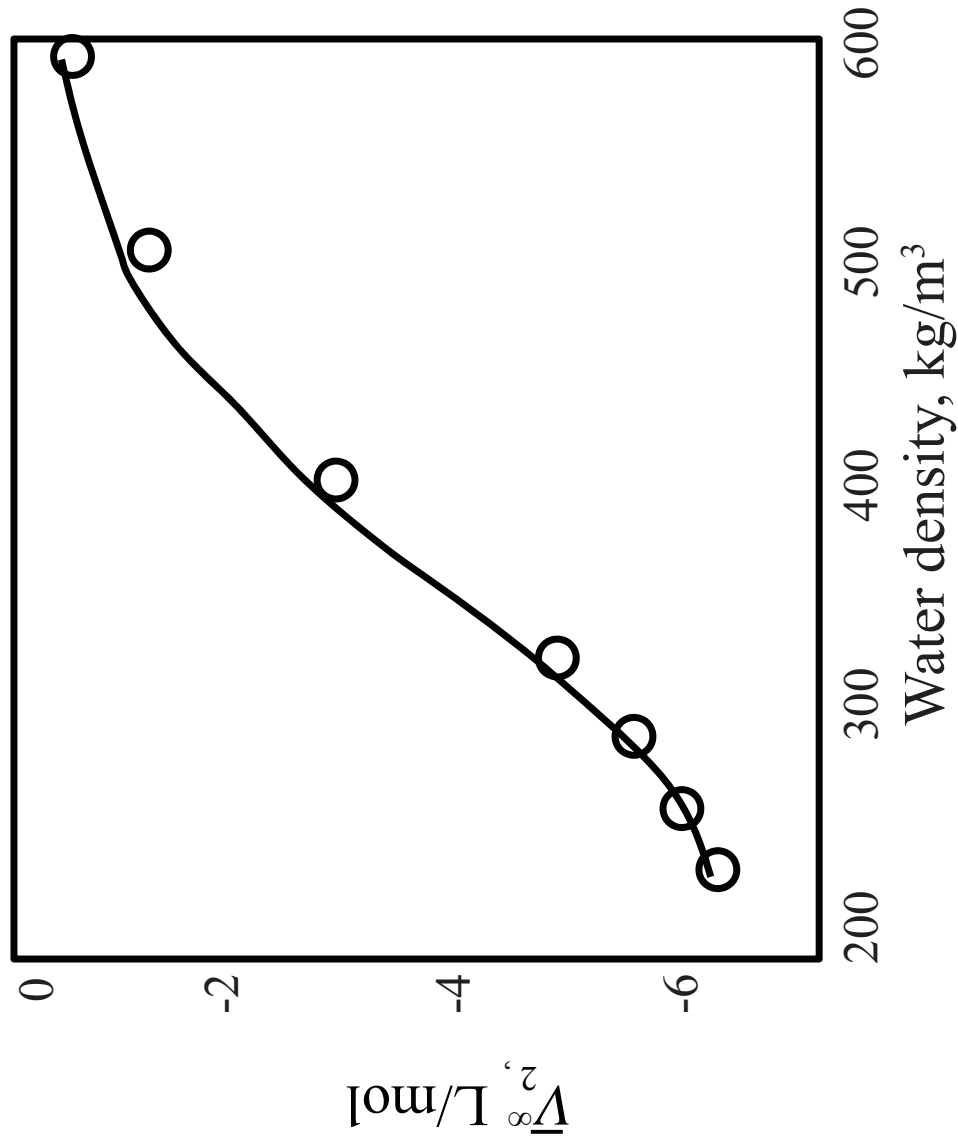


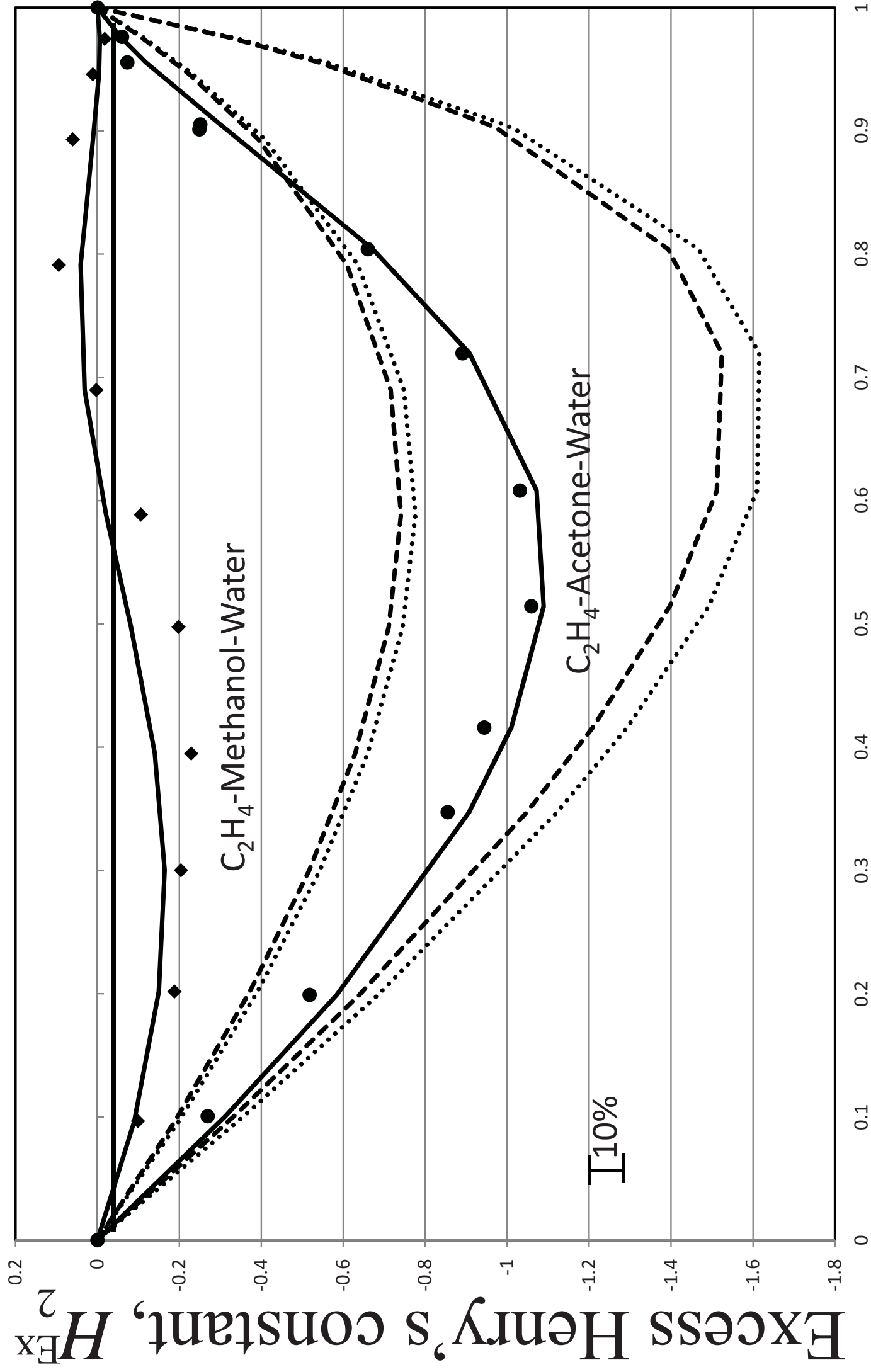












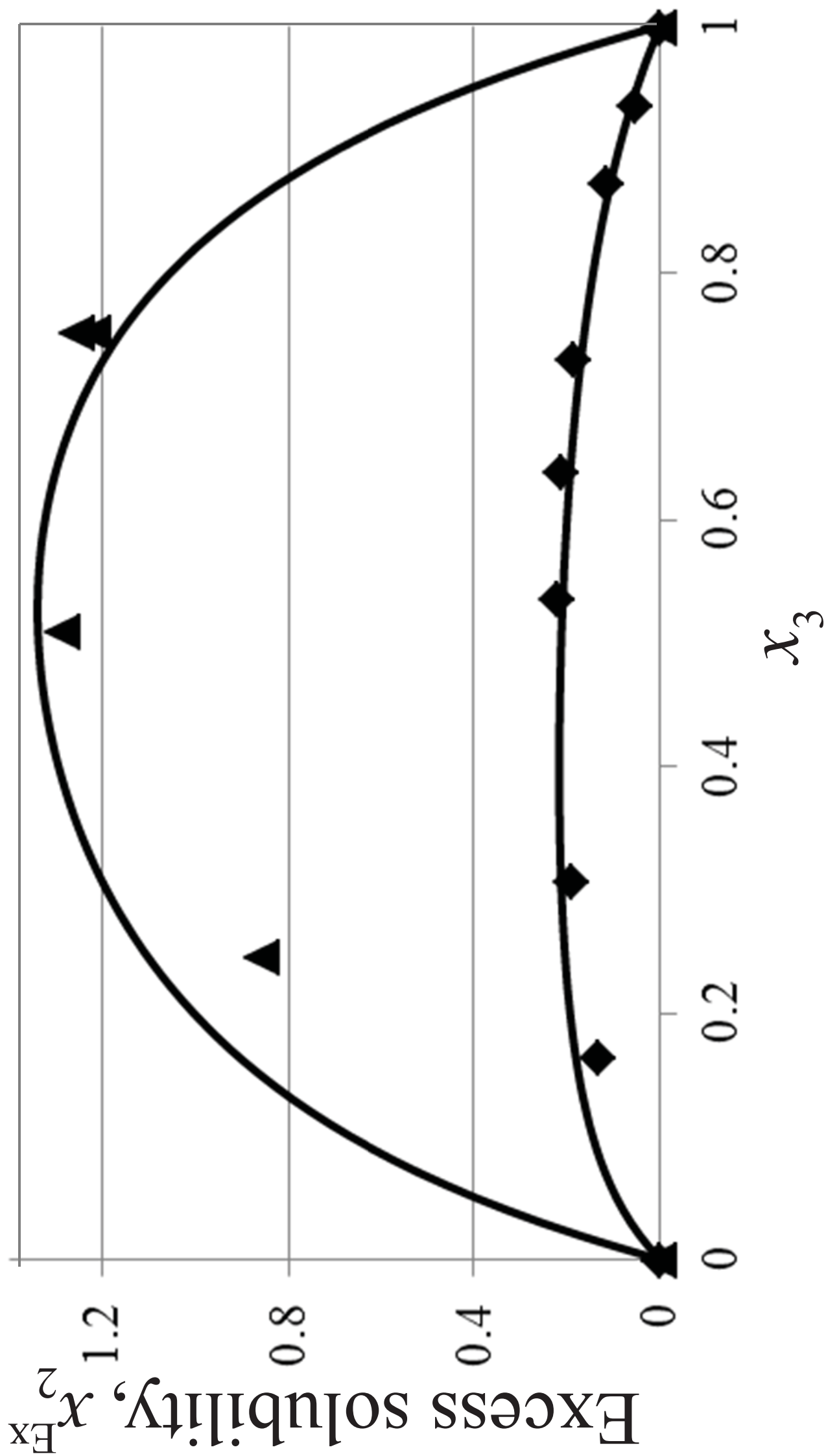
Mole fraction water, x_1

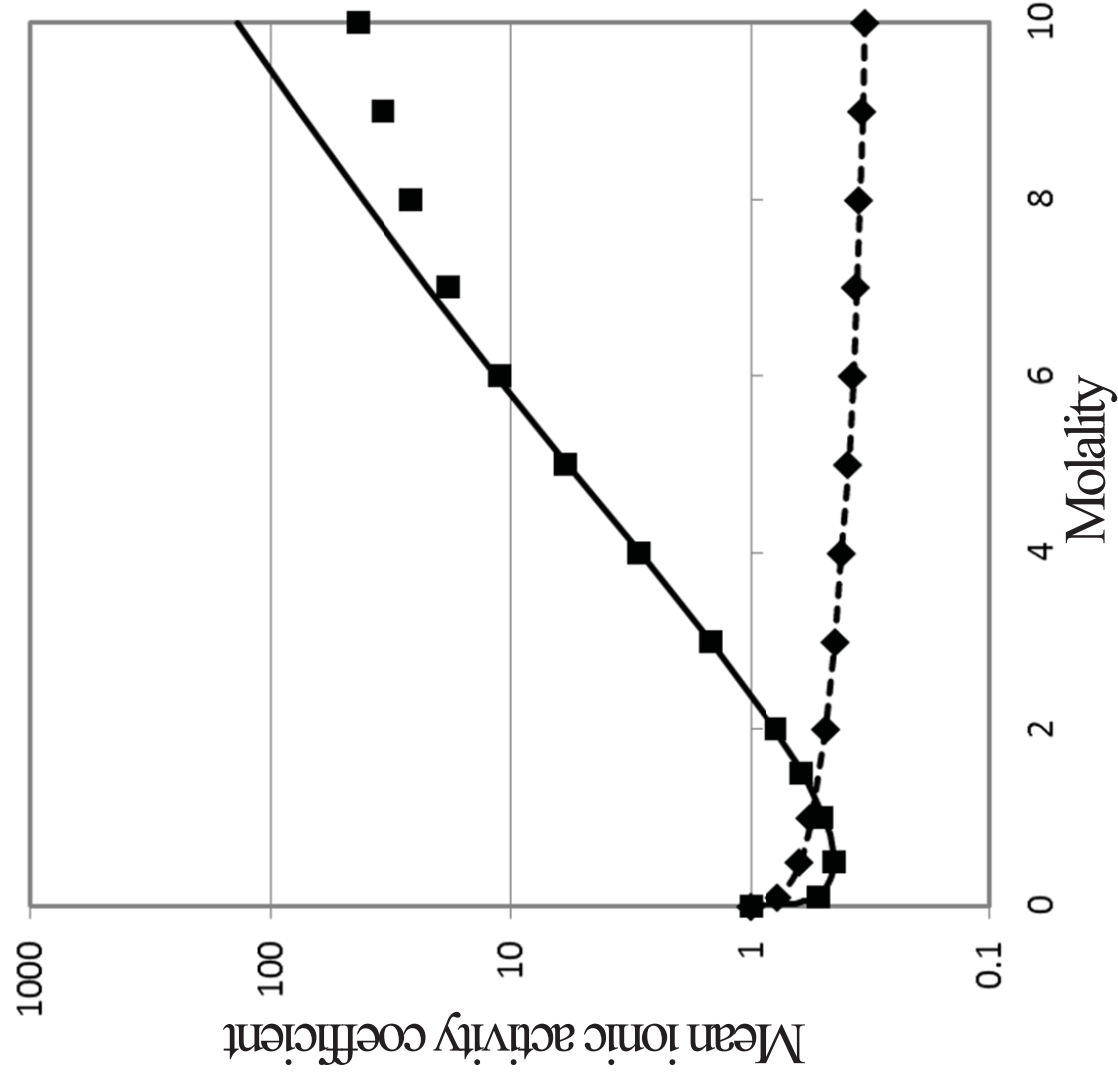
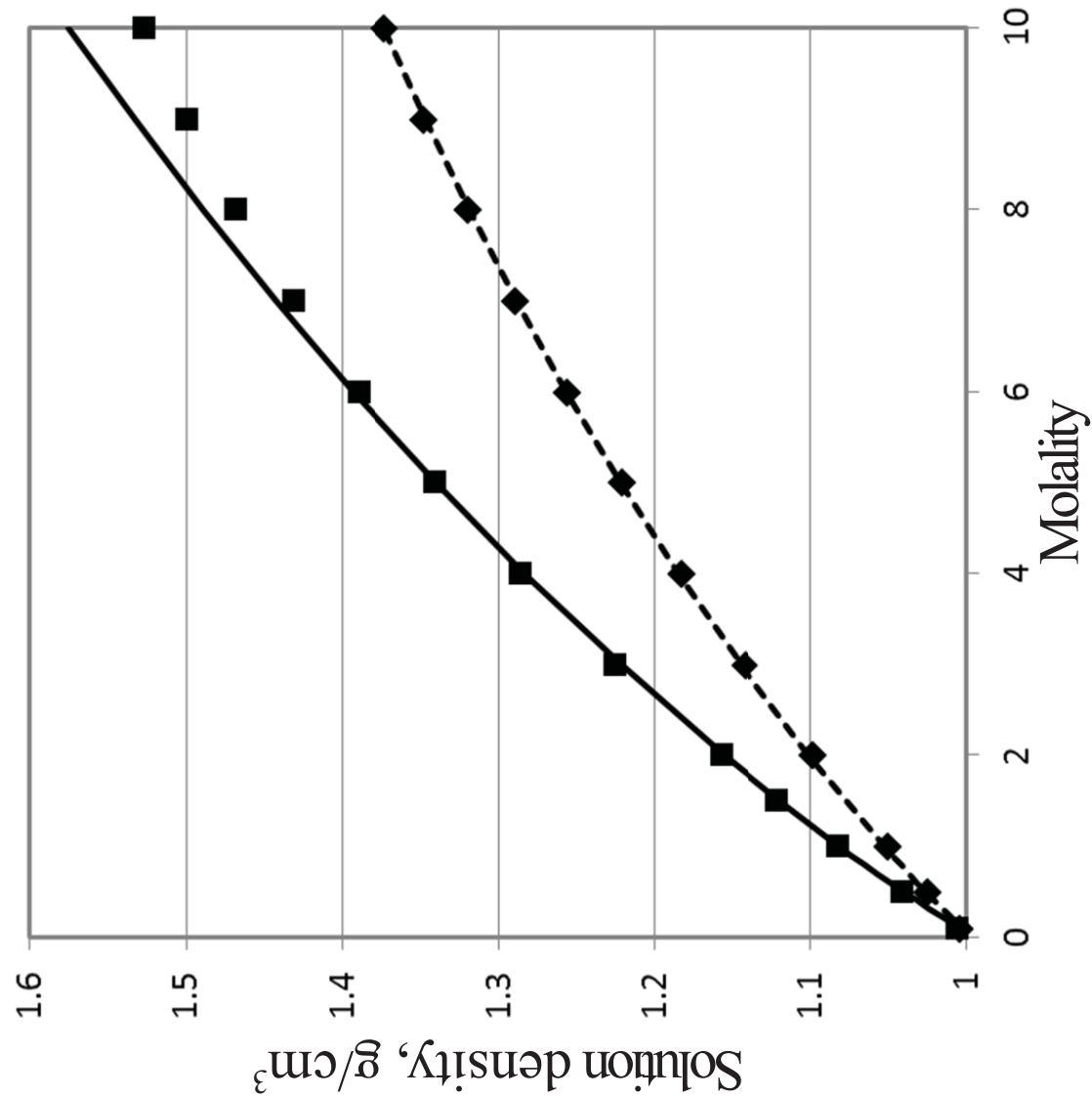
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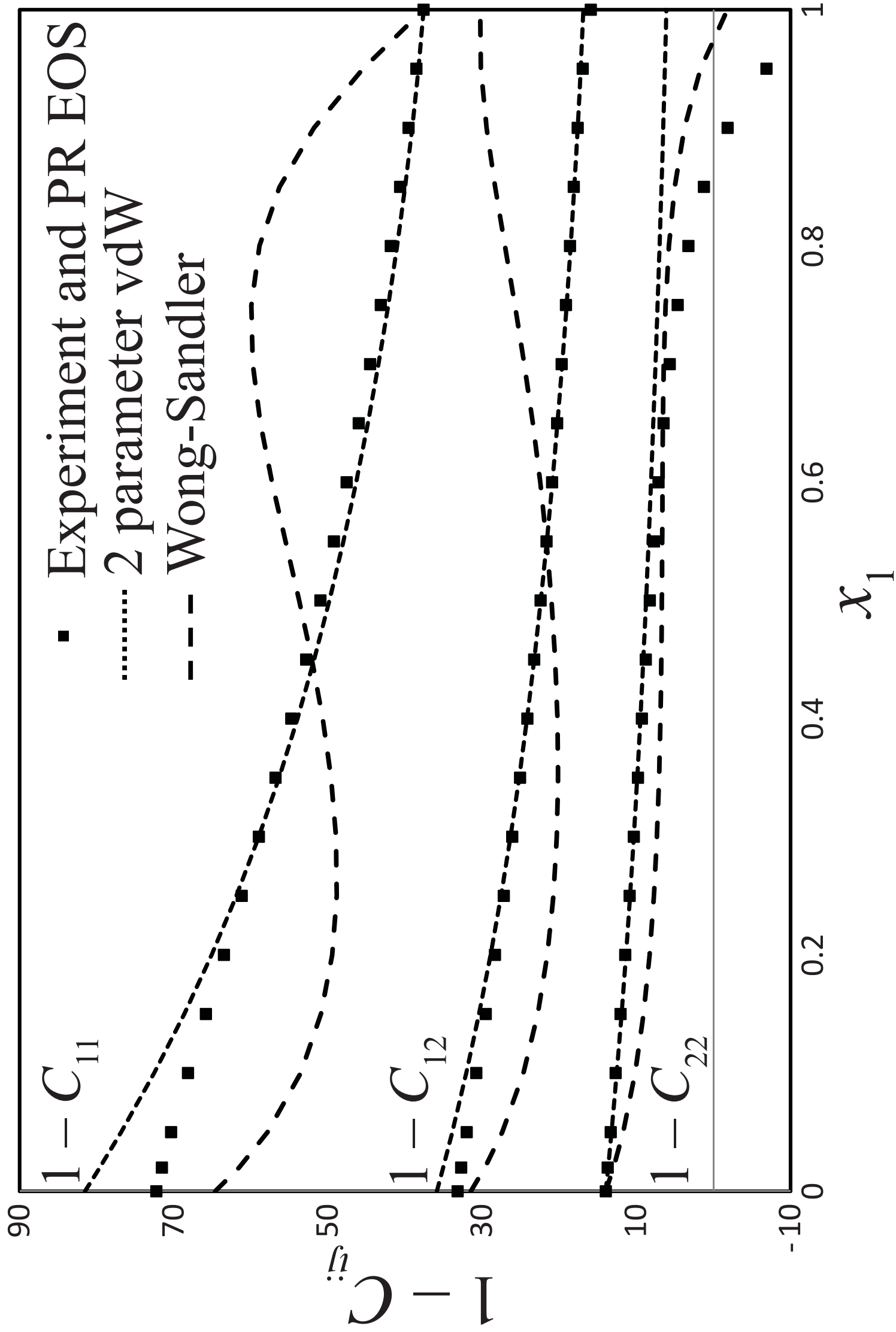
C_2H_4 -Acetone-Water

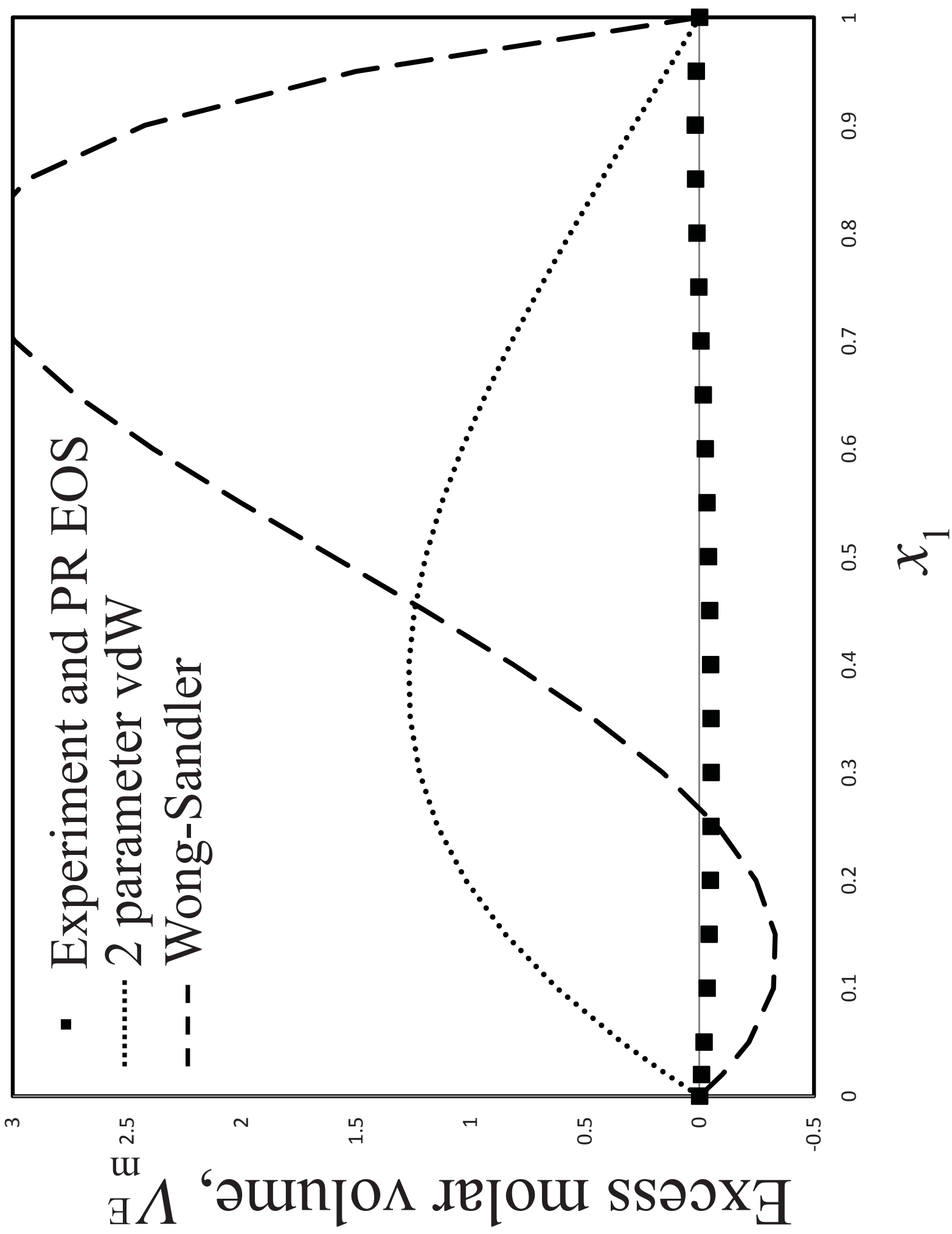
C_2H_4 -Methanol-Water

Excess Henry's constant, H_2^{Ex}









Symbol	Description
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Greek

α_p	Isobaric thermal expansion coefficient (Equation 1.6)
Γ_{23}	Preferential binding parameter (Equation 1.86)
γ_{\pm}	Mean ion molal activity coefficient (Equation 1.92)
γ_i	Lewis-Randall/rational/mole fraction activity coefficient (Equation 1.19)
γ_i^c	Molar activity coefficient
γ_i^m	Molal activity coefficient
Δ	Isothermal-isobaric partition function (Equation 1.28)
ΔG_{ij}	$G_{ii} + G_{jj} - 2G_{ij}$ (Equation 1.93)
ζ_2	$1 + c_i G_{ii} + c_j G_{jj} + c_i c_j (G_{ii} G_{jj} - G_{ij}^2)$ (Equation 1.66)
η_{12}	$c_i + c_j + c_i c_j (G_{ii} + G_{jj} - 2G_{ij})$ (Equation 1.66)
κ_T	Isothermal compressibility (Equation 1.5)
Λ_i	Thermal de Broglie wavelength of specie i
λ_i	Absolute activity of i
μ_i	Chemical potential of component i
μ_{ij}	Chemical potential derivative (Equation 1.1)
ν	Number of cations/anions, $\nu = \nu_+ + \nu_-$
Ξ	Grand canonical partition function (Equation 1.28)
π	Osmotic pressure
ρ	Mass or total number density
ρ_i	Number density of i , $= N_i/V$, see also c_i
ϕ_i	Volume fraction of i , $= \rho_i \bar{V}_i$
ϕ_i	Fugacity coefficient of i (Equation 1.23)
Ω	Microcanonical partition function (Equation 1.28)

Mathematical

$\langle \rangle$	Ensemble or time average
$\{X\}$	Set notation, $\{X_1, X_2, \dots\}$
1	Unit matrix
$ \mathbf{A} $	Determinant of matrix A
\mathbf{A}^{ij}	Cofactor of matrix A
A	Matrix with elements A_{ij}
I	Identity matrix
δ_{ij}	Kronecker delta
δX_i	Instantaneous fluctuation, $X_i - \langle X_i \rangle$
$\langle (\delta X)^2 \rangle$	Mean square fluctuation of a property X

Latin

+	Cation
-	Anion
o	Pure
∞	Infinitely dilute (limiting)
1	Solvent
$1/k_B T$	β
2	Solute
3	Cosolvent/cosolute/additive
$\Delta_r G$	Reaction Gibbs energy (function)
$\Delta_r H$	Reaction enthalpy
$\Delta_r S$	Reaction entropy
δx_{ji}	Preferential solvation parameter (j surrounding i)
$\delta x'_{ji}$	Corrected referential solvation parameter
μVT	Grand canonical ensemble
\hat{X}	Fourier transformed X
\bar{X}_i	Partial molar property of X
a_{\pm}	Mean activity of electrolyte in solution
A	Helmholtz energy (function)
A_i	Aggregate/Multimer of i monomers
a_i	Activity of i
aq	Aqueous solution
c_i	Molarity of i , see also number density, ρ_i
C_{ij}	$\rho \int c_{ij}(r) dr$, DCFI, elements of the C matrix (Equation 1.39)
$c_{ij}(r)$	Direct correlation function
C_p	Constant pressure heat capacity (Equation 1.7)
D	Activity derivative, concentration fluctuation term (Equation 1.73)
f_i	Fugacity of a substance i in a gaseous mixture (Equation 1.21)
G	Gibbs energy (function)
g_{ij}	Radial (pair) distribution function, RDF
G_{ij}	Kirkwood-Buff integral, KBI
H	Enthalpy
h	Planck's constant
H_{ij}	$\rho \int h_{ij}(r) dr = \rho G_{ij}$, TCFI (see below Equation 1.38), or Henry's law constant
$h_{ij}(r)$	Total correlation function, TCF, $g_{ij}(r)-1$
id	Ideal (mole fraction scale)
K	Equilibrium constant
k	Rate constant
k_B	Boltzmann constant

k_H	Henry's law constant, see also H_{ij}
M	Monomer
m	m -value for protein denaturation (see Equation 1.99)
$m_i = c_i / c_1$	(Dimensionless) molality
mix	Mixing process
n	Number of monomers in an aggregate
n_c	Number of components in the system
N_A	Avogadro's number
N_i	Number of entities (usually molecules, atoms, or ions)
N_{ij}	Excess coordination number
NpT	Isothermal-isobaric (Gibbs) ensemble
NVE	Microcanonical ensemble
NVT	Canonical ensemble
p	Pressure
Q	Canonical partition function (Equation 1.28)
r	$ \mathbf{r}_1 - \mathbf{r}_2 $, distance between COM of molecules
R	Gas constant
R_{cor}	Correlation radius (see V_{cor})
S	Entropy
T	Temperature (thermodynamic)
T_m	Melting temperature
trs	Transfer between two phases
U	Internal energy
V	Volume
V_{cor}	Correlation volume (see Equation 1.81)
X^*	Reduced or characteristic quantity X
X_c	Critical X (X is pressure or temperature)
X^E	Excess of X
X^r	Residual of quantity X
x_i	Liquid phase mole fraction composition
X_m	Molar quantity
y_i	Gas phase mole fraction composition, or solute solubility
$z_{+/-}$	Charge of cation/anion

Acronyms

COM	Center of mass
DCF	Direct correlation function
DCFI	Direct correlation function integral
EOS	Equation of state
FF	Force Field

FST	Fluctuation solution theory
FT	Fluctuation theory
GD	Gibbs-Duhem
IG	Ideal gas
KB	Kirkwood-Buff
KBFF	Kirkwood-Buff Force Field
KBI	Kirkwood-Buff integral
LJ	Lennard-Jones
MC	Monte Carlo
MD	Molecular Dynamics
MDF	Molecular Distribution Function
MM	McMillan-Mayer
MW	Molecular Weight
NRTL	Non-Random Two Liquid
OSA	Osmotic stress analysis
OZ	Ornstein-Zernike
PF	Partition function
PI	Preferential Interaction
PMF	Potential of mean force
PS	Preferential Solvation
PY	Percus-Yevick
RDF	Radial distribution function
RK	Redlich-Kister
RISM	Reference interaction-site model
SAFT	Statistical associated-fluid theory
SANS	Small-angle neutron scattering
SAXS	Small-angle X-ray scattering
SI	Symmetric ideal
SPT	Scaled particle theory
TCF	Total correlation function
TCFI	Total correlation function integral
UNIFAC	UNIversal Functional Activity Coefficient
UNIQUAC	UNIversal QUAsiChemical
VDW	van der Waals

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